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**EXPLOSIVE AND PYROTECHNIC
AGING DEMONSTRATION**

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Prepared by

MARTIN MARIETTA CORPORATION

Baltimore, Md. 21227

for Langley Research Center



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Page 17: The attached corrected Thermograph on page 17, Figure 4. - Initial Thermograph for HNS-IIA, should be inserted in the above referenced report, and none of the data presented elsewhere require correction.

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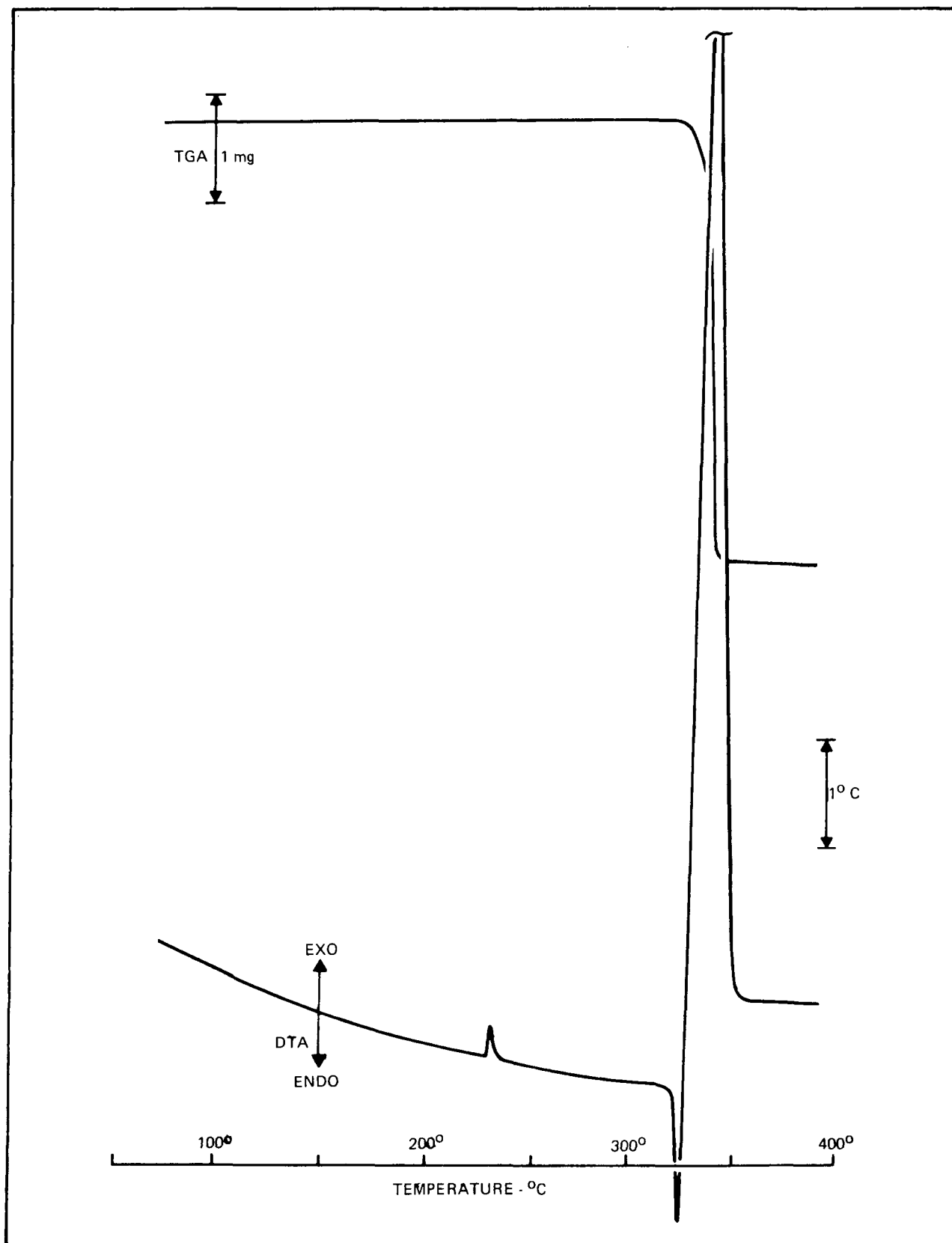


Figure 4. - Initial Thermograph for HNS-IIA

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16. Abstract An 18-month study was conducted to experimentally verify the survivability of five selected explosive and pyrotechnic propellant materials (two primary explosives, one secondary explosive, and two pyrotechnic propellants) when subjected to sterilization (two 64-hour cycles in air at 125°C), and prolonged exposure to space environments (up to 10 years at 10 ⁻⁶ torr vacuum at 66°C). This verification included thermal characterization, sterilization heat cycling, sublimation measurements, isothermal decomposition measurements, and accelerated aging at a preselected elevated temperature. Temperatures chosen for sublimation and isothermal decomposition measurements were believed to be those in which the decomposition processes occurring would be the same as those taking place in real-time aging. The elevated temperature selected (84°C) for accelerated aging was based upon the parameters calculated from the kinetic data obtained in the isothermal measurement tests and was such that one month of accelerated aging in the laboratory approximated one year of real-time aging at 66°C. Results of the study indicate that HNS-IIA, pure PbN ₆ , KDNBF, and Zr/KClO ₄ are capable of withstanding sterilization; dextrinated PbN ₆ and B/KClO ₄ , however, did exhibit changes in thermal characteristics. The accelerated aging tests indicated that unsterilized HNS-IIA and Zr/KClO ₄ can withstand the 10 year, elevated temperature exposure, pure PbN ₆ and KDNBF exhibit small weight losses (less than 2 percent) and B/KClO ₄ exhibits significant changes in its thermal characteristics. Accelerated aging tests after sterilization indicated that only HNS-IIA exhibited high stability.			
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CONTENTS

LIST OF FIGURES	iv
LIST OF TABLES	vi
SUMMARY	1
INTRODUCTION	2
EXPERIMENTAL SECTION	5
Materials	5
Equipment	7
Procedures	9
RESULTS AND DISCUSSIONS	16
HNS-IIA	16
PbN ₆	28
KDNBF	39
Zr/KClO ₄	48
B/KClO ₄	53
CONCLUSIONS	64
REFERENCES	66

LIST OF FIGURES

<u>NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
1.	Mettler Thermoanalyzer	8
2.	Quartz Spring Balance Apparatus	10
3.	Accelerated Aging Apparatus	11
4.	Initial Thermograph for HNS-IIA	17
5.	Thermograph of HNS-IIA After Two Sterilization Cycles	18
6.	SEM Photograph of HNS-IIA Before Sterilization	19
7.	SEM Photograph of HNS-IIA After Sterilization	19
8.	Sublimation Data Plot for HNS-IIA	21
9.	Fractional Decomposition of HNS-IIA	22
10.	Plot of $f(a)$ Versus Time for HNS-IIA	23
11.	Arrhenius Plot for HNS-IIA	24
12.	Accelerated Aging Weight Loss for HNS-IIA	26
13.	Thermograph of HNS-IIA After 183 Days Accelerated Aging	27
14.	Thermograph of Sterilized HNS-IIA After 94 Days Accelerated Aging	29
15.	Initial Thermograph for Dextrinated PbN_6	30
16.	Thermograph of Dextrinated PbN_6 After Two Sterilization Cycles	31
17.	SEM Photograph of Dextrinated PbN_6 Before Sterilization ..	32
18.	SEM Photograph of Dextrinated PbN_6 After Sterilization	32
19.	Sublimation Data Plot for Dextrinated PbN_6	33
20.	Initial Thermograph for Pure PbN_6	36
21.	Thermograph of Pure PbN_6 After Two Sterilization Cycles ..	37
22.	SEM Photograph of Pure PbN_6 Before Sterilization	38
23.	SEM Photograph of Pure PbN After Sterilization	38
24.	Accelerated Aging Weight Loss for Pure PbN_6	40
25.	Thermograph of Pure PbN_6 After 183 Days of Accelerated Aging	41
26.	Thermograph of Sterilized Pure PbN_6 After 66 Days Accelerated Aging	42
27.	Initial Thermograph for KDNBF	43
28.	Thermograph of KDNBF After Two Sterilization Cycles	44

LIST OF FIGURES - Continued

29.	SEM Photograph of KDNBF Before Sterilization	46
30.	SEM Photograph of KDNBF After Two Sterilization Cycles	46
31.	Accelerated Aging Weight Loss for KDNBF	47
32.	Thermograph of KDNBF After 183 Days Accelerated Aging ...	49
33.	Initial Thermograph for Zr/KClO ₄	50
34.	Thermograph of Zr/KClO ₄ After Two Sterilization Cycles ...	51
35.	SEM Photograph of Zr/KClO ₄ Before Sterilization	52
36.	SEM Photograph of Zr/KClO ₄ After Two Sterilization Cycles	52
37.	Accelerated Aging Weight Loss for Zr/KClO ₄	54
38.	Thermograph of Zr/KClO ₄ After 183 Days Accelerated Aging	55
39.	Thermograph of Sterilized Zr/KClO ₄ After 94 Days Accelerated Aging	56
40.	Initial Thermograph for B/KClO ₄	57
41.	Thermograph of B/KClO ₄ After Two Sterilization Cycles	58
42.	SEM Photograph of B/KClO ₄ Before Sterilization	62
43.	SEM Photograph of B/KClO ₄ After Sterilization	62
44.	Thermograph of B/KClO ₄ After 183 Days Accelerated Aging ..	63

LIST OF TABLES

<u>NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
I.	Sublimation Results for HNS-IIA	20
II.	Isothermal Decomposition Results for HNS-IIA	25
III.	Sublimation Results for Dextrinated PbN_6	34
IV.	Isothermal Decomposition Results for Dextrinated PbN_6	34
V.	Accelerated Aging Parameters for Pure PbN_6	39
VI.	Isothermal Decomposition Results for KDNBF	45
VII.	Isothermal Decomposition Results for Zr/KClO_4	48
VIII.	Thermal Events of Sterilized and Unsterilized B/ KClO_4 Propellant	59
IX.	Weight Loss (as fractional Decomposition, α) During Sterilization	59
X.	Sublimation Results for B/ KClO_4	61

EXPLOSIVE AND PYROTECHNIC AGING

DEMONSTRATION

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SUMMARY

An 18-month study was conducted to experimentally verify the survivability of five selected explosive and pyrotechnic propellant materials (two primary explosives, one secondary explosive, and two pyrotechnic propellants) when subjected to sterilization and prolonged exposure to space environments (up to ten years at 10^{-6} torr vacuum at 66°C).

To accomplish this, each material was:

1. thermally characterized by simultaneous differential thermal analysis and thermogravimetric analysis (DTA/ TGA);
2. tested for the ability to withstand two sterilization cycles of 64 hours each at 125°C ;
3. tested to measure its sublimation characteristics;
4. subjected to isothermal decomposition measurement tests to determine kinetic data, and;
5. aged at a preselected elevated temperature to obtain definitive accelerated-aging data.

The initial thermograph recorded for each material served as both a reference standard for the comparison of the thermal characteristics after sterilization and accelerated aging, and as a guide for the selection of the temperature ranges used in sublimation and isothermal decomposition measurement tests. Temperatures chosen were believed to be those in which the decomposition processes occurring would be the same as those taking place in real-time aging. The elevated temperature selected (84°C) for accelerated aging was based upon the parameters calculated from the kinetic data obtained in the isothermal measurement tests and was such that one month of accelerated aging in the laboratory approximated one year of real-time aging at 66°C .

Results of the study indicate that two of the materials (one secondary explosive and one pyrotechnic propellant) appear to be capable of withstanding sterilization and/or accelerated aging, hence should be capable of surviving prolonged exposure to space environments.

INTRODUCTION

Future long-term missions, such as deep space probes, planetary explorations and long-term Earth-orbital missions, will require spacecraft pre-launch sterilization heat cycling and exposure to deep space environments for periods up to 10 years. Explosive- and propellant-actuated devices used to perform in-flight mechanical functions must survive these exposures and still perform reliably. More specifically, the chemical components (i. e., the explosive and pyrotechnic propellant materials) in the devices must maintain their initial performance characteristics throughout the mission.

When subjected to relatively high sterilization temperatures (two 64-hour cycles at 125°C) and on prolonged exposure to space environments (10 years at 66°C^* under 10^{-6} torr), these chemical components could undergo several physical changes. For example, materials having relatively high vapor pressures could sublime away from initiating interfaces, thus creating voids and possible functional failures; in particular, exposed material at the open ends of mild detonating fuse leads (MDF) might evaporate or sublime, creating voids and the possibility of failure. Or, after inflight storage at an elevated spacecraft temperature for periods of up to 10 years, sufficient thermal decomposition of the materials could occur to affect performance of the device. Further, many ordnance devices contain several explosives, and any material that would melt during sterilization or flight could be subjected to eutectic mixing during cooling, thereby affecting performance.

To determine whether such deleterious affects will occur in long-term, deep space missions, each material had to be tested. Since heat sterilization is accomplished in a few days, laboratory tests duplicating the sterilization requirements can be performed quite easily¹⁻⁶. However, since it is not practical to conduct real-time aging and performance testing of devices or analytical (chemical) testing of components to determine their survivability and reliability after several years; an accelerated aging testing technique must be used.

Previous and recent studies being conducted on the "accelerated aging" of explosives and propellants⁷⁻¹⁰ have been directed at determining the effects of age on the performance of devices or propellants and at establishing the maximum safe storage life. However, in these studies, "accelerated aging" is the storage of an explosive- or propellant-actuated device at some rather arbitrarily chosen temperature above ambient (typically, 50° to 80°C) under ambient pressure, for periods ranging from 1 to 3 years. The philosophy of such an approach is that since heat is a primary contributor to chemical decomposition, than if the items survive storage at an elevated temperature for a particular length of time, they will survive for longer periods of time at lower temperatures.

The authors gratefully acknowledge the valuable assistance of Mr. G. Fair of Martin Marietta Laboratories for experimental work during this investigation.

*Caused by solar radiation or onboard radioisotope thermoelectric generators (RTGs).

The most quantitative accelerated aging method proposed thus far is based on a modification of the Arrhenius reaction rate equation¹¹. This method assumes that if a material survives a certain length of time at some elevated temperature, survival time increases by a factor of between 2.7 and 2.9 for every 10°C decrease in temperature. Conversely, it is assumed that the reaction rate for all materials increases by a factor between 2 and 3 for each 10°C rise in temperature.

But neither the modified-Arrhenius approach nor any other current accelerated aging method considers the possibility that a change may occur in the activation energy of the critical degradation process with temperature change.

An accelerated aging procedure can be valid only if the critical degradation process occurring at the elevated test temperature is exactly the same process that occurs under actual conditions. The relationship between the rate of a degradation process and temperature may not be a single linear relationship; rather, two or even more linear relationships may develop. An example is the case of PETN, where the plot of log (% weight loss) against reciprocal temperature results in two straight lines with the break occurring at the melting point¹². In such a case, any accelerated aging above the melting point would be meaningless because the test would be monitoring a reaction completely different from the one actually occurring in aging. Another example is seen in the thermal decomposition of ammonium perchlorate (AP). Below approximately 300°C, AP undergoes decomposition such that only 30% of the starting material is decomposed; above 300°C, the reaction goes to completion (100%) with a different activation energy. Therefore, it is extremely important that the temperature selected for the accelerated aging tests be within the temperature range applicable to the chemical reaction occurring in real-time aging.

The processes involved in aging can be described in terms of solid-state kinetics. It is possible to deduce a meaningful and correct aging mechanism from data on the parameters relating to the physicochemical properties of the materials (e.g., thermal-decomposition kinetics, sublimation kinetics, phase-change characteristics, change-of-state phenomena, etc.). These decomposition and sublimation data can be used to predict material losses for deep space exposure periods up to ten years. When these kinetic data are not available, an analytical approach can be used to determine these parameters. Since explosive and propellant materials stored for years in a vacuum at some elevated temperature will undergo degradation through sublimation and/or thermal decomposition, the rates of these two processes constitute the parameters of major interest.

The rate at which a material decomposes thermally is designated by the rate constant, k , the thermal dependence of which is given by:

$$k = A \exp (-E/RT)$$

where k is expressed in units per second, E is the activation energy in kcal per mole, T is the absolute temperature, and A is an experimentally determined frequency factor. If the fractional decomposition, a , under isothermal conditions, can be determined as a function of time, t , then k can be evaluated. Several equations have been derived to describe the complete $a - t$ curves¹³ such that accurate linear plots can be obtained up to $a = 0.99$. For our purposes, we are interested in a values of 0.10 maximum decomposition or less, permitting use of the simple expression:

$$t = \ln (1 - a) / k$$

for all cases.

A similar approach has been used by Green, et. al¹⁴. In an effort to make long-term predictions of propellant compatibility based on accurate short-term data, the rate of metal ion concentration buildup in the propellant was measured. From this data, the kinetic rate expression was established and an Arrhenius plot ($\log k$ vs $1/T$) was used to determine the temperature dependence of the rate constant. Using this information, Green was able to predict the concentration of metal buildup over a given period of time or the time required for the metal buildup concentration to reach a given level. Furthermore, they showed that the maximum storage temperature to limit the metal buildup to a specified concentration over a given duration could be calculated, thus, the maximum allowable storage temperature could be projected.

The degree of sublimation exhibited by a material can be determined by the Langmuir method¹⁵ using the expression:

$$G = \frac{P}{17.14} \sqrt{\frac{M}{T}}$$

where G is the rate of sublimation in gm per cm² per sec, P is the vapor pressure in torr, M is the molecular weight, and T is the absolute temperature. If the vapor pressure of a material cannot be extracted from experimental data, it can be derived from the vapor pressure equation¹⁶ expressed as:

$$\log P = A + E/4.576T$$

where A and E are experimentally determined constants (A the frequency factor and E the activation energy associated with the process) and T is the absolute temperature.

By using data available from the literature and these analytical expressions on explosive and pyrotechnic propellant materials, a selection of

candidate materials most likely to survive sterilization and long-term deep space aging has been made by Gorzynski and Maycock¹⁸ under contract to NASA Langley Research Center (Contract No. NAS1-10698). Their study contained a list of those chemicals considered most likely to meet all mission requirements. The objective of the Martin Marietta Laboratories' program, then, was to verify experimentally the survivability of these materials. To achieve this objective, the thermal decomposition and sublimation characteristics of each of these materials was determined in the first part of the program so that a meaningful elevated temperature could be chosen for the accelerated-aging studies. Using this approach, we obtained definitive accelerated-aging data pertaining to a 10-year flight time in a laboratory time span of about 10 months.

EXPERIMENTAL SECTION

Materials

The materials selected for testing under this program were chosen from lists of candidate materials recommended by Gorzynski and Maycock¹⁸.

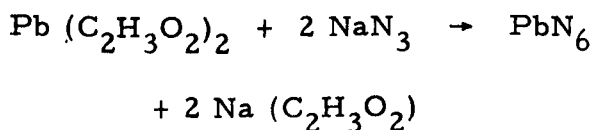
From these lists materials were selected for each of the functional categories of compounds - primary explosives, secondary explosives and pyrotechnic propellants. The specific selections for each category are:

- Primary explosives: lead azide and potassium dinitrobenzofuroxan
- Secondary explosives: hexanitrostilbene
- Pyrotechnic propellants: Zr/KClO₄ and B/KClO₄.

To assure validity of the results, an effort was made to obtain samples from well-characterized, high-quality lots of materials. Specific details for each sample material are given below.

Lead azide (PbN₆). - a sample of dextrinated lead azide (containing 5% dextrin) was obtained from Picatinny Arsenal, N.J. The sample was from Lot No. 52-127 manufactured by du Pont in 1952 and was purchased under military specification MIL-L-3055. This batch of material has been extensively tested (19,20) and characterized by Picatinny Arsenal.

Pure lead azide was prepared in-house for sterilization and accelerated-aging measurements to replace the dextrinated PbN₆. This was prepared from "CP" grade lead acetate and sodium azide according to the reaction:



The PbN_6 , was then filtered, washed, vacuum dried and characterized by thermal analysis.

Potassium dinitrobenzofuroxan (KDNBF). - The KDNBF sample was also obtained from Picatinny Arsenal, N.J. and is from SMUPA lot 1 B7172. Manufactured in 1966, this material was purchased under Military Specification MIL-P-50486 (MU). This material Lot has been used in several studies^{19, 20}, and it therefore, is well characterized.

Hexanitrostilbene (HNS). - A sample of high purity commercially prepared HNS-IIA was obtained from the Naval Ordnance Laboratories, White Oak. The sample was from Lot X-773 (NOL), manufactured by Chemtronics, Inc. (Lot No. 36-45) in October, 1971, using the Shipp and Kaplan²¹ process. The "IIA" designation indicates that the material has been recrystallized to a controlled bulk density from a mixed solvent refluxed over HNS-I.

Other properties are:

Bulk Density	0.55 g / cc
Water Soluble Materials	0.02%
Surface Volatiles	0.01%
Insoluble Materials	0.02%
Particle Size	80% between 50 and 100 microns by coulter counter.
Impurities	High purity, possible trace NaCl as result of manufacturing process.

Zirconium - potassium perchlorate (Zr/KClO_4). - Primarily a 50/50 mixture of powdered zirconium metal and potassium perchlorate with a small percentage of Viton binder, this pyrotechnic propellant was obtained from the Hi-Shear Corporation. The sample is from Lot No. 021,

manufactured January 6, 1972. Exact details of the composition and manufacturing process are proprietary information of the manufacturer.

Boron - potassium perchlorate (B/KClO₄). - A sample of B/KClO₄ propellant was supplied by the Hi-Shear Corporation. The material was from Lot No. 055, manufactured April 23, 1973. The composition was approximately 20/80 proportion of B and KClO₄ with a small percentage of ferric oxide and Viton binder. Exact details of composition and method of manufacture process are proprietary information of the manufacturer.

Equipment

Thermoanalyzer - mass spectrometer. - Preliminary screening and isothermal decomposition measurements of the sample materials were conducted using a Mettler TA-1 Thermoanalyzer (Figure 1) capable of performing simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA). In differential thermal analysis (DTA), the sample under evaluation and an appropriate reference material are heated or cooled at a linear rate, and the temperature difference between them is measured. Since all of the phenomena that can occur to a sample as it is heated are accompanied by energy changes, then the resulting DTA thermograms may be used to characterize or identify the material under study in terms of its physical and chemical thermal reactions. DTA, therefore, can be used to observe changes in the thermal behavior of a material resulting from alterations to its physical or chemical properties prior to testing.

Thermogravimetric analysis (TGA) is the study of material weight changes, measured either as a function of time under isothermal conditions (static method) or as a function of temperature while the sample is heated at a linear rate (dynamic method). Since thermal decomposition and sublimation are both weight-loss processes, the extent of decomposition or sublimation of a material and its dependence on time, temperature, atmosphere, and pressure thus can be determined.

The thermoanalyzer is capable of testing samples from one to 500 mg. In this case, 5 mg samples were used for HNS, Zr/KClO₄, and B/KClO₄, while 2 mg samples were used for PbN₆ and 3 mg samples for KDNBF. Samples may be tested in vacuum or any gaseous atmosphere, static or flowing, up to one atmosphere pressure. Heating may be isothermally controlled or at a programmed rate (0.2 to 100°C/Min) up to 1600°C. A 10°C/Min heating rate was used for all materials except KDNBF which was 6°C/Min. Maximum sensitivity of the TGA is 10 μg of weight change, while for the DTA it is 0.2°C/in. The maximum TGA sensitivity was used for all samples, but the DTA sensitivity used was 1.0°C/in. All samples were vibrated to achieve optimum packing of the sample in the crucible.

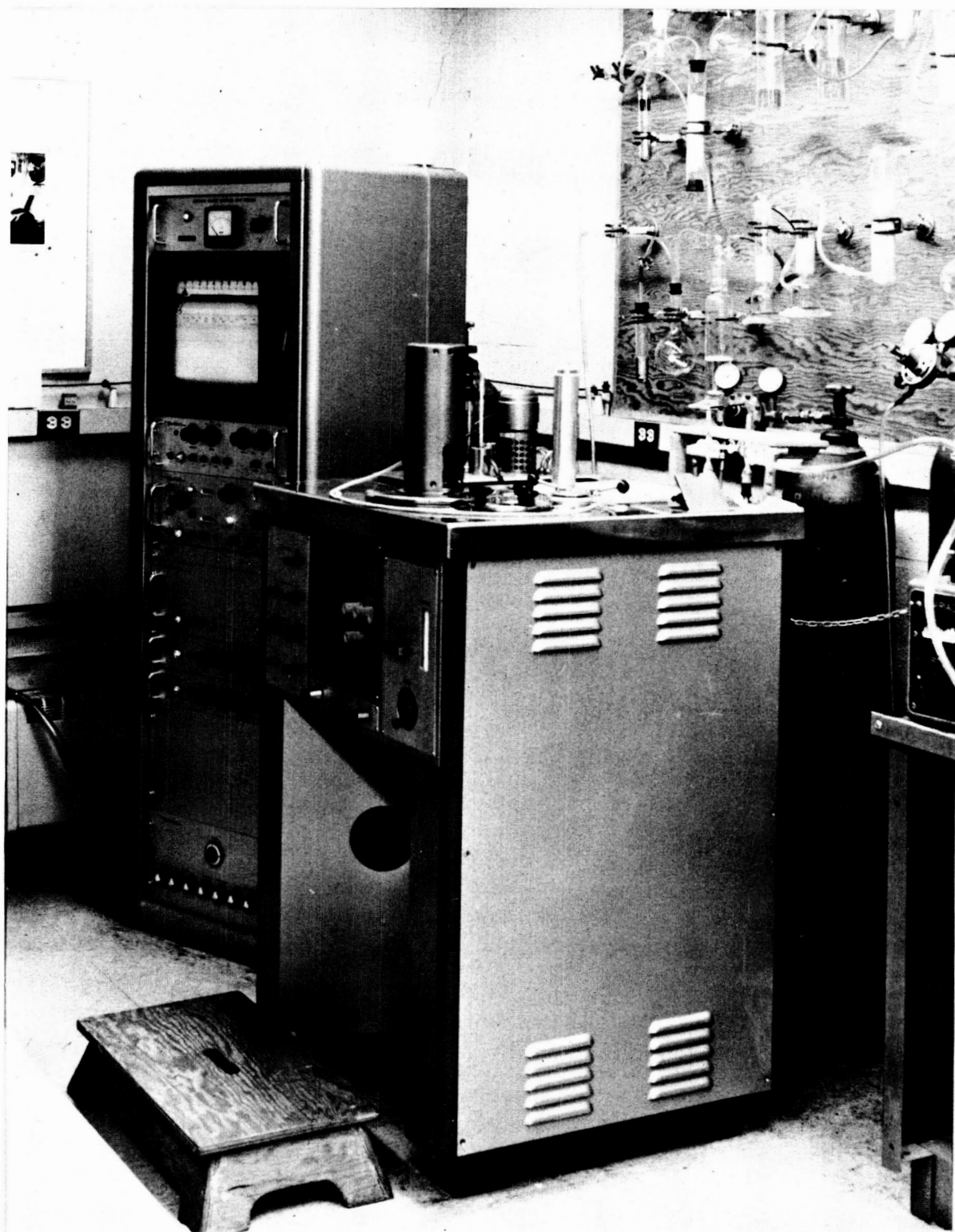


Figure 1. - Mettler Thermoanalyzer

Coupled to the thermoanalyzer is a Balzers QMG 101A Quadrupole Mass Spectrometer which is used for EGA (evolved gas analysis) identification of decomposition products. The Balzers is mounted directly in the Mettler thermoanalyzer, so that immediate identification of evolved products can be obtained. EGA of the effluent gases was performed during the highest and lowest isothermal decompositions for each of the four test environments to provide a comparison to identify differences in decomposition mechanisms attributable to different test temperatures and atmospheres. It was found, however, that the concentration of the decomposition products was so small as to be beyond the detection limits of mass spectrometer.

Quartz spring balances. - Measurements of the sublimation rates were made using quartz spring balances as shown in Figure 2. The quartz springs were calibrated for dimensional length change in terms of weight change per unit of length change (e. g. , mg/mm). A small fused quartz bucket containing the sample was hung on each spring. These quartz buckets were suspended within an electronically regulated furnace. Five such set-ups were used so that the sublimation rate of each material, with the exception of KDNBF, could be measured simultaneously at five different temperatures.

All of the samples were maintained under high vacuum through continuous pumping with a Varian Vac Ion pump, after initial evacuation with a Varian cryogenic absorption pump. The use of this pumping system, rather than the conventional mechanical pump and oil diffusion pump system, eliminated the possibility of oil vapors entering the system and any consequent oil-sample reactions.

The quartz spring balance apparatus was also used for accelerated-aging measurements on samples of unsterilized materials since it provided a method of continuously monitoring the weight of a sample.

Oil bath. - Accelerated aging of the samples for thermoanalysis was performed by suspending pyrex tubes containing the samples in a circulating oil bath thermostatically controlled at 84°C. The pyrex tubes were connected to a vacuum manifold and were evacuated using the same pumping system used with the quartz spring balance apparatus. See Figure 3.

Miscellaneous equipment. - Sterilization of the sample materials was performed in air in a conventional laboratory oven capable of maintaining $125 \pm 3^\circ\text{C}$. Sample weighings were performed using a Mettler H-16 balance.

Procedures

Preliminary screening. - An initial simultaneous DTA/TGA test was conducted on each material to provide a characteristic control thermograph to be used as a reference standard for evaluating the effects of sterilization and aging upon the individual materials. By comparison of peak shape, height and temperature, changes in the materials can be detected. These measurements were conducted in a flowing atmosphere of dry nitrogen with calcined aluminum oxide being used as the DTA reference material. To

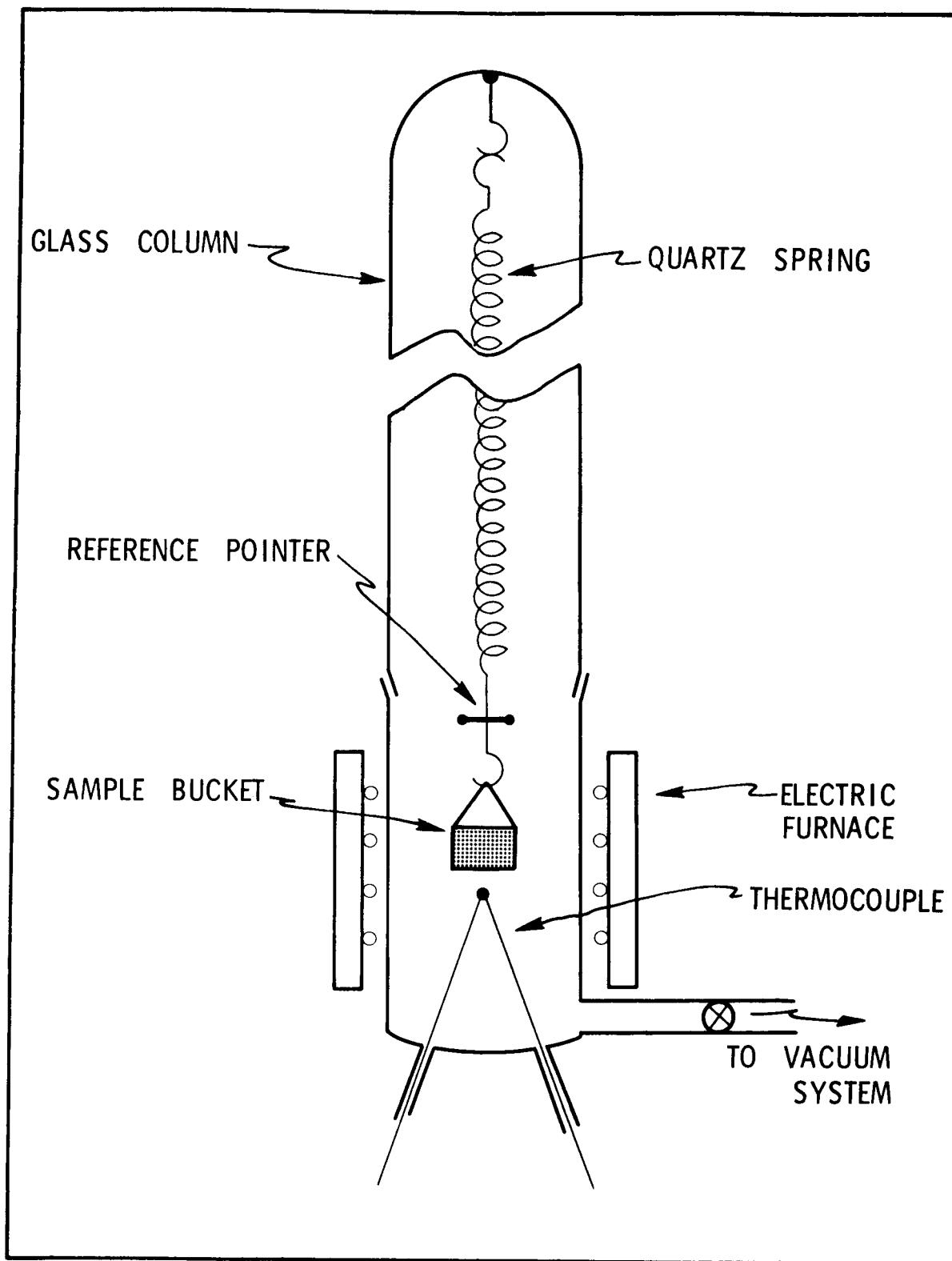


Figure 2. - Quartz Spring Balance Apparatus

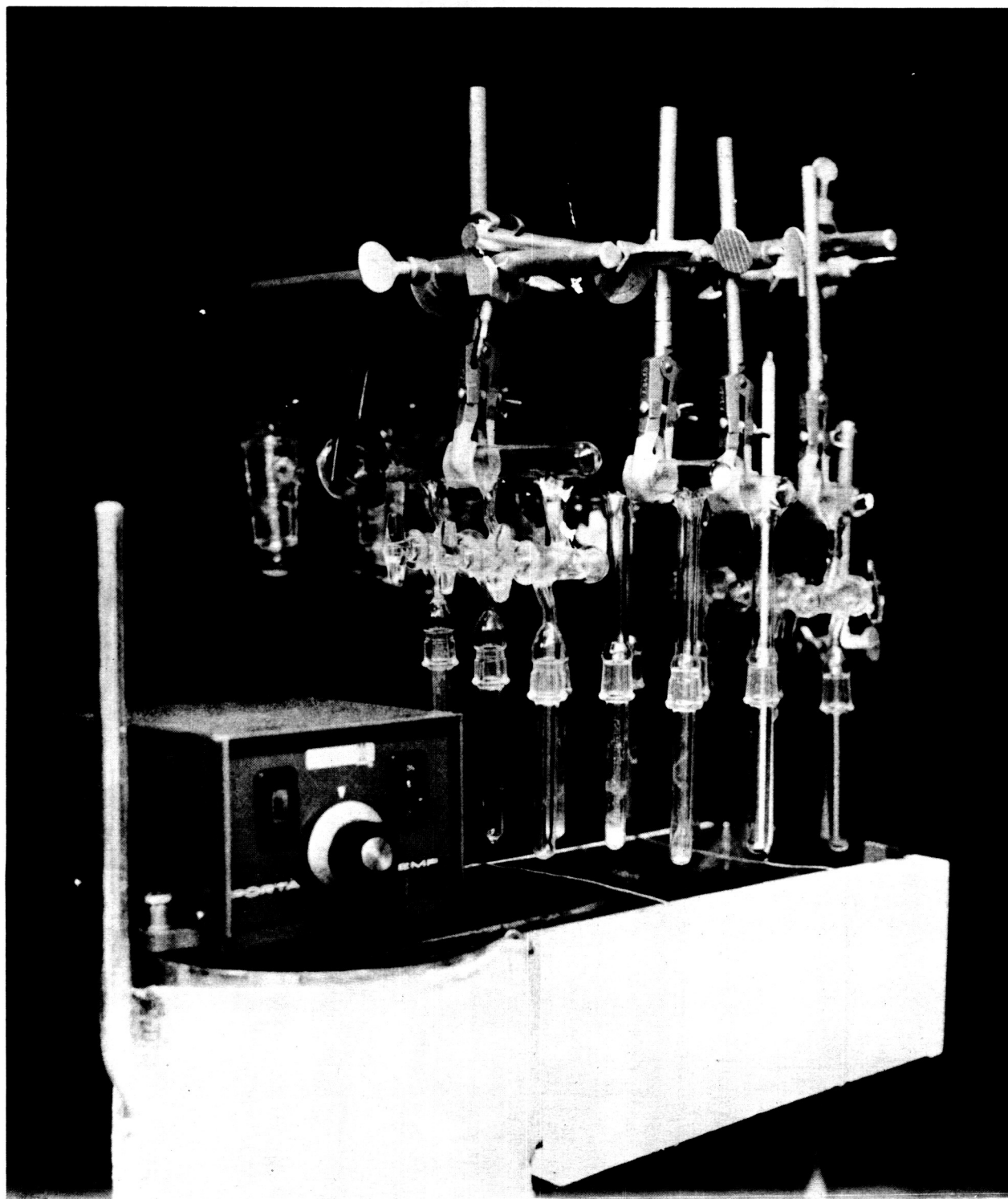


Figure 3. - Accelerated Aging Apparatus

provide an internal temperature standard, several tin pellets (A DTA temperature standard issued and certified by the National Bureau of Standards in cooperation with the International Confederation for Thermal Analysis.) were placed in the reference cup. The melting tin pellets result in a small exothermic peak on the DTA trace with an onset temperature known to be 230°C.

In addition, these thermographs were used to select the temperature at which the isothermal decomposition and sublimation measurements would be performed.

Sterilization. - Each material was subjected to two 64-hour heat sterilization cycles in a conventional laboratory oven at $125 \pm 3^\circ\text{C}$ in air. Following each cycle, a simultaneous DTA/TGA test was performed on a sample of each material. The results of these tests were compared with those obtained during the preliminary screening.

Additionally, the morphology, of each material before and after each sterilization cycle was examined through the use of a scanning electron microscope.

Sublimation. - Measurements of the sublimation rates were made on each of the materials, with the exception of KDNBF, using the quartz spring balances. The system was designed to measure the sublimation rate of each material at five different temperatures simultaneously. A small fused quartz bucket containing a known amount of sample with a known exposed surface area was suspended from each of the five quartz spring balances into five electronically regulated furnaces. The samples were evacuated to $\sim 10^{-6}$ torr and then raised to and maintained at the test temperature by the regulated furnaces.

Test temperatures were selected after examination of the thermographs obtained during the preliminary screening of the materials. Criterion for selection was to choose the maximum sublimation temperature such that the amount of thermal decomposition taking place would be negligible. These temperatures ranged between 100°C and 200°C. Periodic reading were taken to measure the dimensional changes of the quartz springs as a result of the weight change of the sample. The results of these measurements were plotted against time and the rate of sublimation was calculated.

For materials composed of a single chemical compound, the vapor pressure was calculated using the Langmuir expression:

$$G = \frac{P}{17.14} \sqrt{\frac{M}{T}}$$

Additionally, the heats of sublimation were determined for these materials whose vapor pressure could be calculated using the vapor pressure equation:

$$\log P = A + E/4.576T$$

and curves of $\log P$ vs reciprocal temperature.

Isothermal decomposition. - Initial DTA/TGA analyses of each material provided characteristic thermographs to be used as reference standards. Any changes in the chemical or physical properties of a material produced (for example, by sterilization) would be detected as changes in the thermographs when compared to the standards. The standard thermographs also were used to select the temperatures for the isothermal TGA studies. This approach to temperature selection ensured that the temperatures chosen could be reached with an appropriate heating ramp before any significant decomposition took place. Following the initial test at the first selected temperature, for each successive test, the temperature was adjusted to provide the most meaningful isothermal data.

The isothermal decompositions of each material also were performed in the Mettler Thermoanalyzer 1. Each material was tested at five different temperatures for each of the four specified test environments: (1) closed volume vacuum, (2) continuously pumped vacuum, (3) closed volume air, and (4) open to the atmosphere. These four conditions simulate the environmental exposures possible with both occluded and vented systems.

Isothermal decomposition data is in the form of a set of curves depicting weight loss as a function of time at different temperatures. These curves first are normalized in terms of fractional decomposition (α) as a function of time, t . For each temperature, the α - t data is analyzed according to the equation:

$$t = \ln(1 - \alpha) / k$$

whereby linear plots are obtained if $\ln(1 - \alpha)$ is plotted against t . The slopes of these lines are equal to k , the rate constant for the respective temperature. The k values are plotted as $\ln k$ vs reciprocal temperature, since

$$\ln k = \ln A - E/RT$$

The slope of the resultant line will be equal to E/R , where E is the activation energy of the decomposition process. This analytical analysis assumes that the topochemistry of the decomposition is known. If not, a more general analytical model should be used. This is possible if the rate equation can be expressed in the general form:

$$f(\alpha) = kt$$

when k is the rate constant and a_n, a_{n+1} are values of the fractional decomposition a at times t_n and t_{n+1} respectively. Thus,

$$F(a_{n+1}) - F(a_n) = k(t_{n+1} - t_n).$$

For a different temperature, but for the same values of a :

$$F(a_{n+1}) - F(a_n) = k'(t'_{n+1} - t'_n).$$

A plot of $\ln(t_{n+1} - t_n)$ against T^{-1} should be linear and have a slope of E/R .

To illustrate the use of these techniques, the analysis of the kinetics data for the isothermal decomposition of HNS-IIA under continuously pumped vacuum is described below. (Curves are shown on pages 20-24.)

From the Arrhenius plot ($\ln k$ vs. $10^3/T$) for HNS-IIA under these test conditions, the slope of the line is measured to be 16.7. Using this value we obtain the activation energy :

$$E_a = \text{slope} (R) = 16.7 (1.99) = 33.2 \text{ kcal.mole}^{-1}$$

From the function a vs. time plot (in this case, $1 - (1 - a)^{1/3}$ vs. t), the rate constant at 230°C is determined to be $4.225 \times 10^{-5} \text{ sec}^{-1}$. Using this value and the slope of the Arrhenius plot, it is possible to calculate the rate constant at 66°C by:

$$k_2 = k_1 e^{\text{slope} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad \text{thus}$$

$$K_{66^\circ} = 4.225 \times 10^{-5} e^{16.7 (1.937 - 2.949)} = 4.454 \times 10^{-12} \text{ sec}^{-1}$$

Therefore, the fractional decomposition (a) for one year at 66°C is:

$$a = 1 - e^{-kt}, \quad \text{where } t = \text{one year} = 3.15 \times 10^7 \text{ sec,}$$

if $kt \ll 1$ then $a = kt$ and,

$$a = 4.45 \times 10^{-12} (3.15 \times 10^7) = 1.40 \times 10^{-4}$$

For one month accelerated aging to be equivalent to one year at 66°C, the rate constant must be

$$k_A = \frac{a}{t}, \text{ where } t = \text{one month} = 2.59 \times 10^6$$

then

$$k_A = \frac{1.40 \times 10^{-4}}{2.59 \times 10^6} = 5.40 \times 10^{-11} \text{ sec}^{-1}$$

thusly,

The accelerated aging temperature (T_A) is then calculated

$$\begin{aligned} \frac{1}{T_A} &= 2.949 - \frac{1}{\text{slope}} \ln \frac{k_A}{k_{66^\circ}} \\ &= 2.949 - \frac{1}{16.7} \ln \frac{5.40 \times 10^{-11}}{4.45 \times 10^{-12}} \\ &= 2.799 \end{aligned}$$

$$T_A = 357^\circ\text{K or } 84^\circ\text{C}$$

Decomposition reaction rates and activation energies have been tabulated over the temperature range studied for each test environment and compared to determine whether the same reaction is occurring over the temperature range of interest for the accelerated-aging studies.

Accelerated aging. - Early in the isothermal decomposition measurements, it became apparent that many of accelerated aging temperatures were in the 75°C - 90°C range. This is not unusual considering that all of the materials are of the metastable type, which decompose rapidly after initiation. Since the accelerated aging temperatures fall within the same general range and the use of a single aging temperature would greatly simplify the experimental apparatus set-up and operation, it was decided to test all of the materials at the same accelerated aging temperature. Therefore, each of the unsterilized specified explosive and pyrotechnic materials was aged in a vacuum of less than 1×10^{-6} torr at a temperature of 84°C. The 84°C temperature was chosen because the degradation process rate of each material at that temperature is accelerated to the extent that approximately one month of accelerated aging equaled one year of real-time aging. Four of the materials (the exception being B/KClO₄) were set up in the quartz spring balances so the weight change could be continuously monitored during aging

while the samples were held at aging temperature by the electronically controlled furnaces.

In addition, samples of each of the materials were stored in pyrex tubes to provide samples for periodic thermal analysis. These samples were maintained at the aging temperature by immersion in an oil bath. Both sets of samples were maintained under vacuum by a VacIon pump to eliminate the possibility of pump oil-sample interaction. At each appropriate test-time point (as determined by the continuously monitored quartz spring balance measurements), a simultaneous DTA/TGA test was performed on the aged material. These were compared with the control thermograph to observe the changes.

After the unsterilized accelerated aging tests were in progress and preliminary data was obtained, one material was selected from each of the functional categories (i. e. , primary explosive, secondary explosive, pyrotechnic propellant) for limited sterilized accelerated aging. The materials selected were pure PbN_6 , HNS and Zr/KClO_4 . Samples of each of these materials were sterilized (two heat soaks of 64 hours each at 125°C) then aged under vacuum in the oil bath with the unsterilized samples for simultaneous DTA/TGA testing.

RESULTS AND DISCUSSIONS

Hexanitrostilbene (HNS-IIA)

Preliminary screening of HNS-IIA (hexanitrostilbene) was conducted and the results are shown in Figure 4 , the initial thermograph for HNS-IIA. Important features of the thermograph are the peak at 230°C which is the result of melting of the tin in the reference cup, the melting of the HNS-IIA at 322°C just prior to decomposition, and the main decomposition exotherm temperature occurring at 344°C . This thermograph was used as the control standard for comparison with thermographs taken after sterilization and aging.

Following each of two sterilization cycles (125°C for 64 hours each) simultaneous DTA/TGA tests were repeated. The thermograph after two sterilization cycles is shown in Figure 5. This figure is essentially identical to the control thermograph with the melting point of HNS-IIA occurring at 323°C and the main decomposition exotherm temperature occurring at 342°C . Apparently, no significant change has taken place in the HNS-IIA as a result of sterilization.

SEM micrographs taken before and after sterilization to determine morphology changes are shown in Figures 6 and 7, respectively. No morphological change is apparent upon examination of the micrographs.

Sublimation measurements of HNS-IIA were conducted at temperatures from 82°C to 150°C for a test period of 216 hours. No measurable weight loss occurred at the lower temperatures, however, at 132°C ,

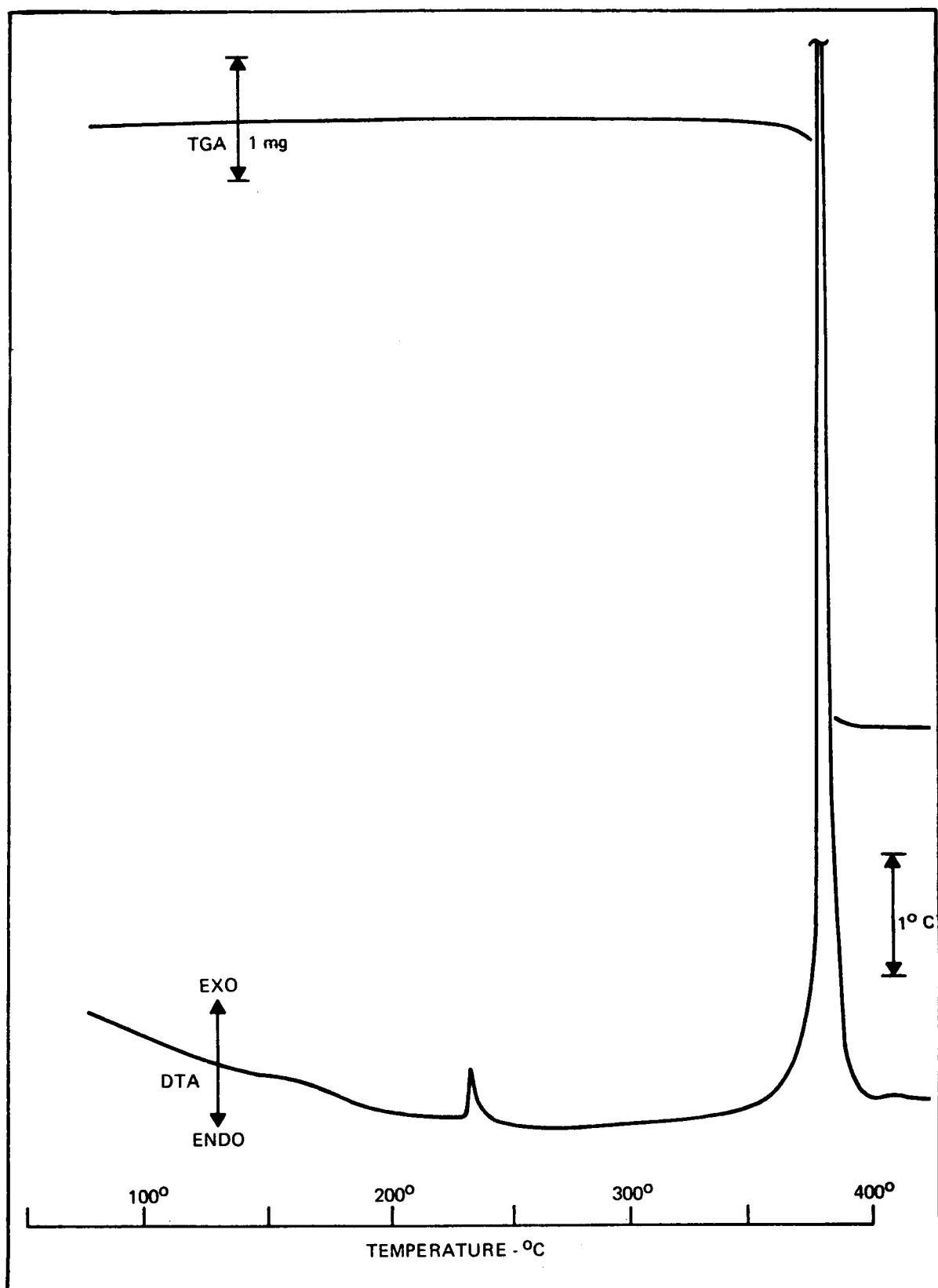


Figure 4. - Initial Thermograph for HNS-IIA

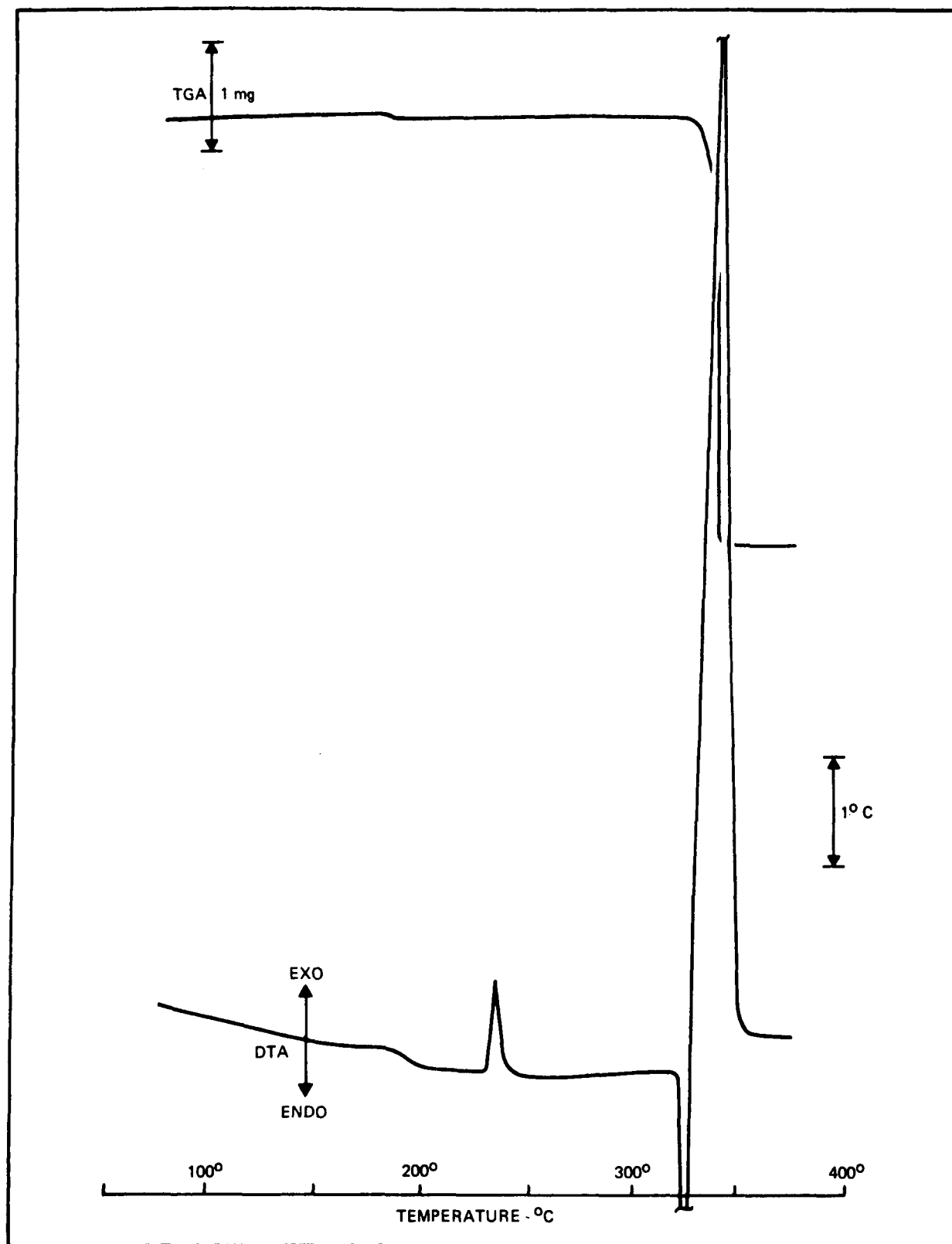


Figure 5. - Thermograph of HNS-IIA After Two Sterilization Cycles

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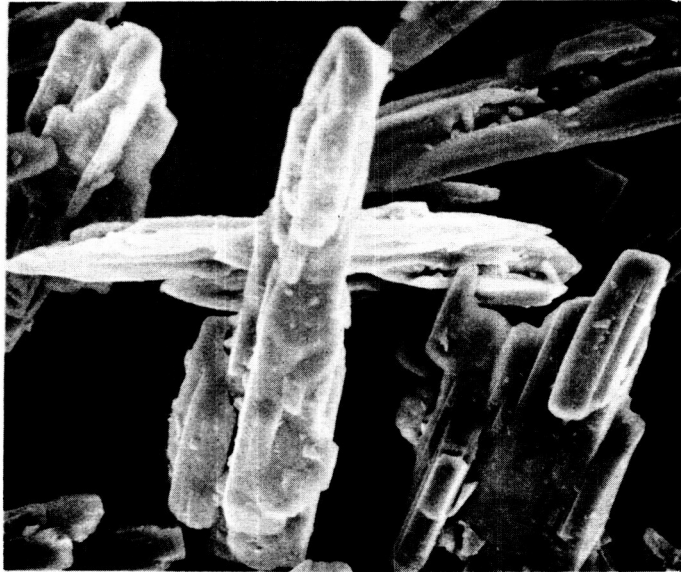


Figure 6. - HNS-IIA—Before Sterilization (300X)

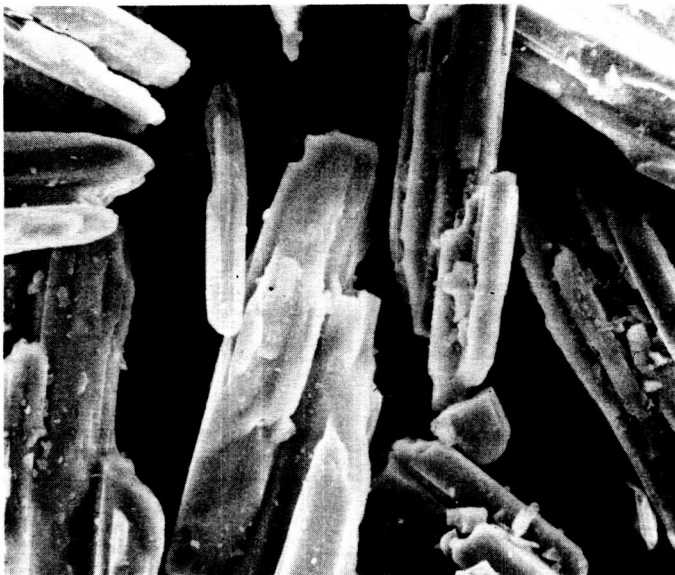


Figure 7. - HNS-IIA—After Sterilization (2X, 64 hr, 125° C) (300X)

139°C and 150°C weight loss data was obtained. These data are shown in Figure 8. Weight loss rates, sublimation rates, and vapor pressures calculated from these data are given in Table I.

TABLE I. - SUBLIMATION RESULTS FOR HNS-IIA

Temp. °C	Wt. Loss Rate mg/hr.	Sublimation ^G gm/cm ² /sec	Vapor ^P Press torr.
132	6.24×10^{-4}	2.63×10^{-10}	4.28×10^{-9}
139	2.75×10^{-2}	1.02×10^{-8}	1.67×10^{-7}
150	3.75×10^{-2}	1.41×10^{-8}	2.34×10^{-7}

Isothermal decomposition measurements were conducted for HNS-IIA over the temperature range of 230° to 300°C using the four test environments : (1) continuously pumped vacuum, (2) closed volume vacuum, (3) closed volume air, and (4) open to the atmosphere.

Analysis of the isothermal decomposition data for HNS-IIA tested in a continuously pumped vacuum test environment is described below.

First, the weight loss as a function of time was normalized by expressing it in terms of the fractional decomposition, a . A plot of a vs time (t) as a function of temperature is shown in Figure 9.

Next, a function of a (i.e. $\ln(1-a)$, $(1-a)^{\frac{1}{2}}$, $1 - (1-a)^{1/3}$, etc.) was selected which would produce linear plots when plotted against t . A set of curves for HNS-IIA tested in a continuously pumped vacuum environment is shown in Figure 10. The function of a in this case was $1 - (1-a)^{1/3}$. Since these lines fit the equation:

$$f(a) = kt$$

the slope of these lines equals the rate constant (k) at each temperature.

Finally, an Arrhenius plot of $\ln k$ versus the reciprocal temperature ($10^3/T$) (Figure 11) was prepared. The slope of this line according to the Arrhenius equation, $k = A \exp(E/RT)$, equals E/R , where E is the activation energy of the decomposition process and R is the international gas constant.

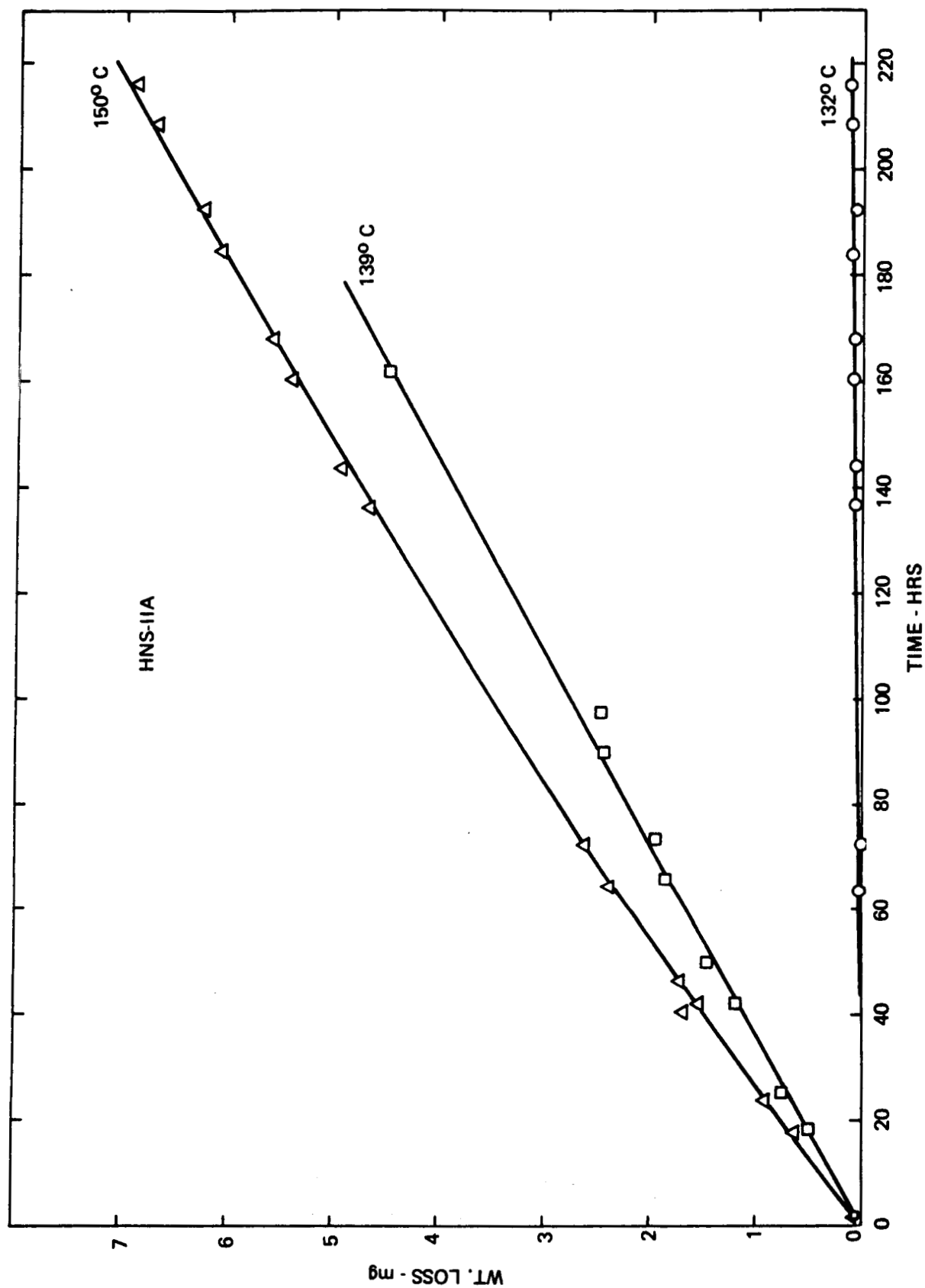


Figure 8. - Sublimation Data Plot for HNS-IIA

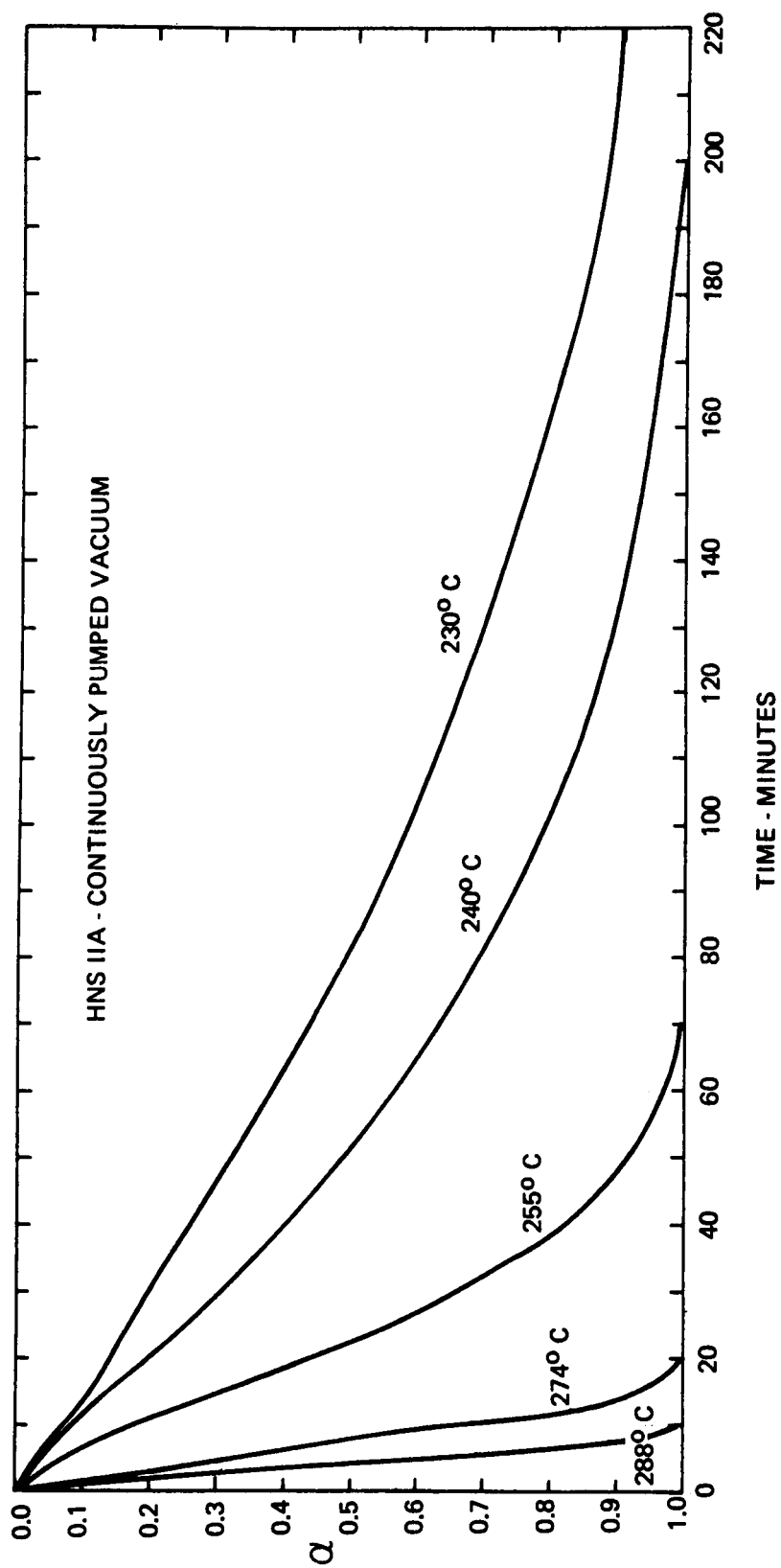


Figure 9. - Fractional Decomposition of HNS-IIA

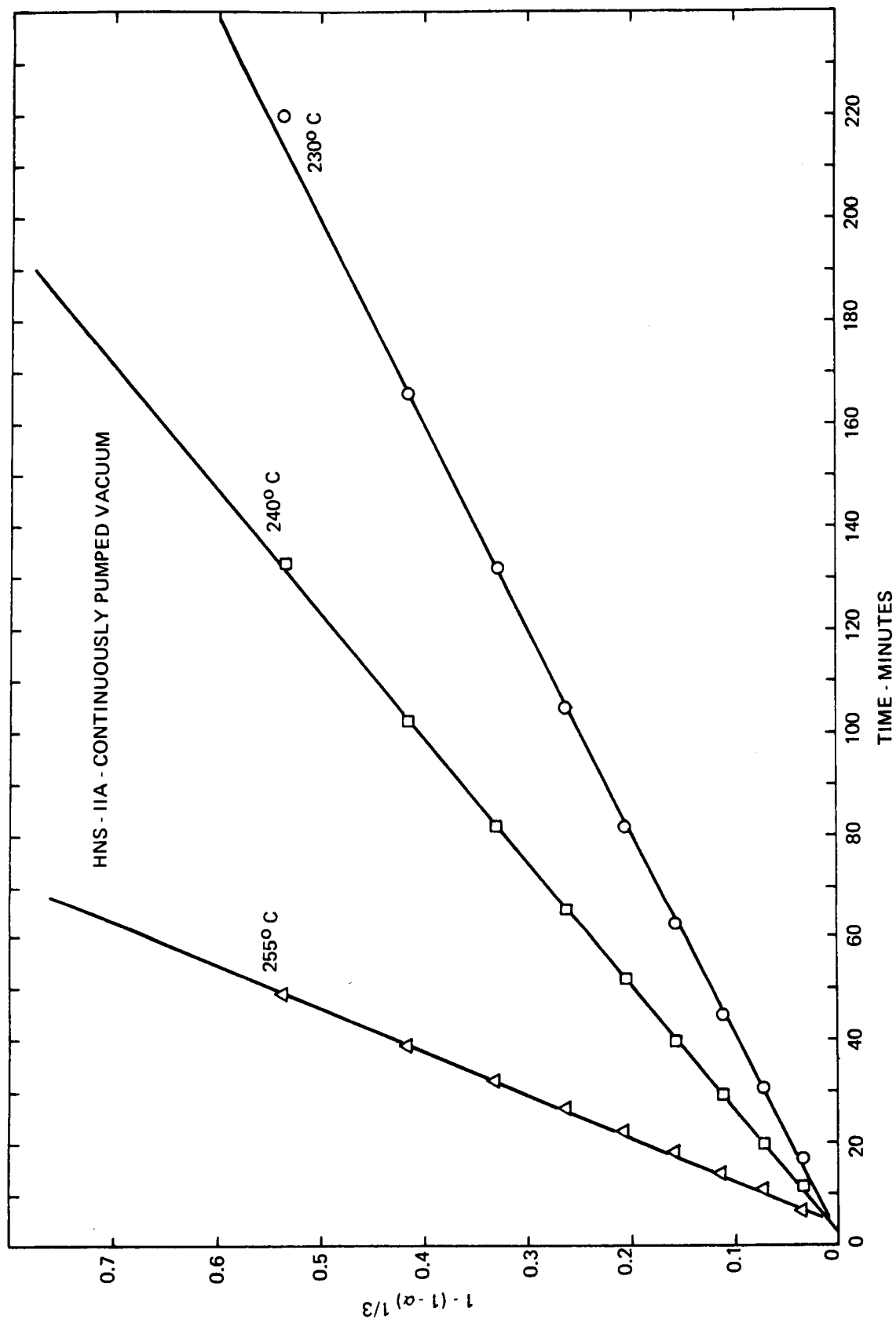


Figure 10. - Plot of $f(\alpha)$ Versus Time for HNS-IIA

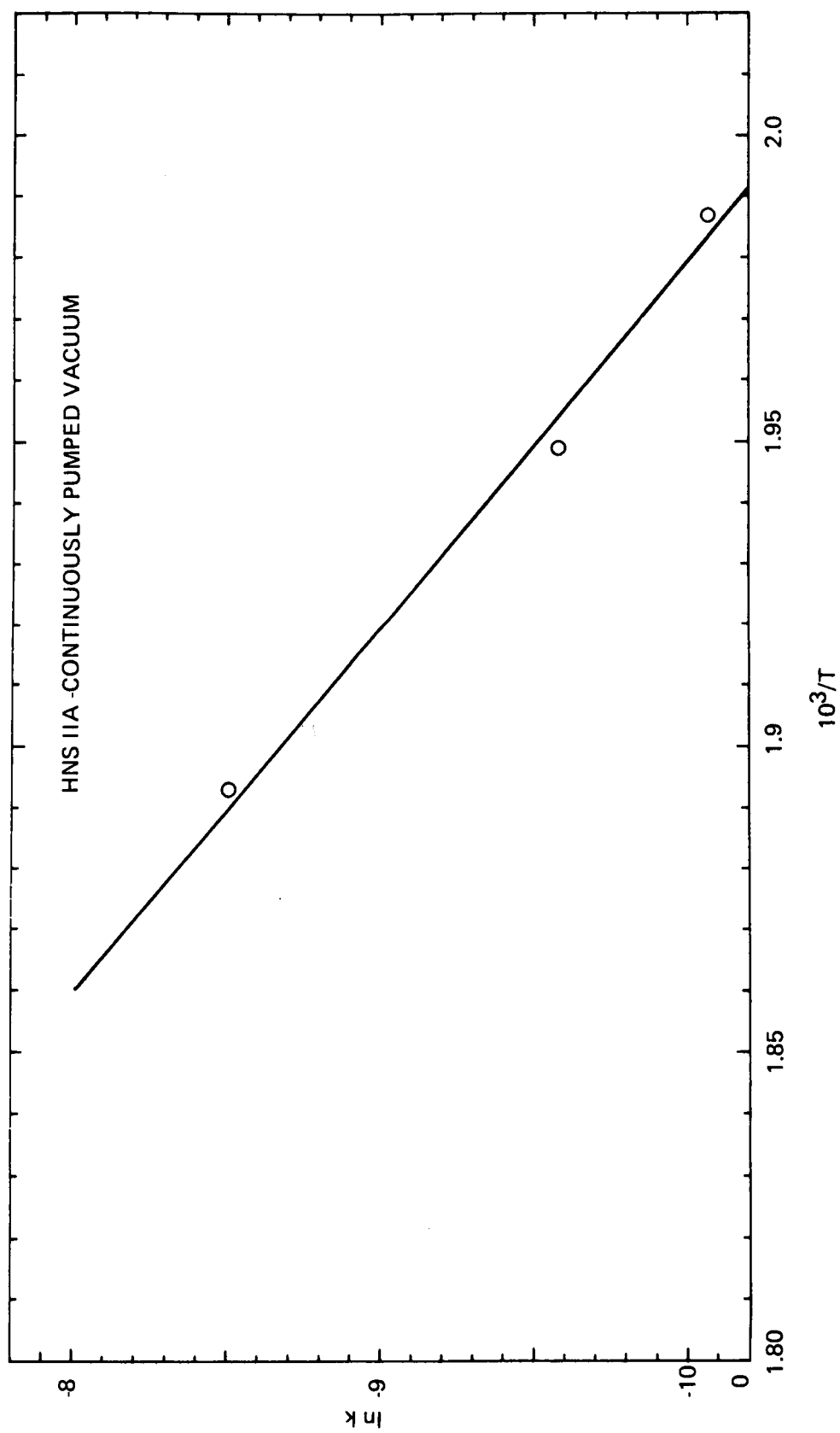


Figure 11. - Arrhenius Plot for HNS-IIA

Using the rate constants and activation energy thus determined, the accelerated-aging parameters can be calculated by the method outlined in the Procedures section.

A summary of the experimental results obtained for HNS-IIA are given in Table II.

TABLE II. - ISOTHERMAL DECOMPOSITION RESULTS FOR HNS-IIA

Conditions	Activation Energy Kcal/ mole	k @ 66°C sec ⁻¹	^a One Year	T _A Accel. Aging Temp °C
Cont. Pumped Vac.	33.2	4.45 x 10 ⁻¹²	1.40 x 10 ⁻⁴	84°
Closed Vol. Vac.	48.6	1.34 x 10 ⁻¹⁵	4.22 x 10 ⁻⁸	78°
Open Air	39.2	1.71 x 10 ⁻¹⁵	5.39 x 10 ⁻⁸	81°
Closed Vol. Air	11.8	1.10 x 10 ⁻⁶	-	123°

The results obtained for the closed volume air environment are somewhat confusing. For example, the rate of weight loss at 230°C was greater than at 240°C. During the first several hours of testing, however weight increases were observed. It was also learned that if the vent to the thermoanalyzer was closed completely, gas pressure changes within the instrument would produce corresponding weight changes in the TGA curve. Moreover, the possibility of reaction of the decomposition products with the HNS-IIA further complicates the process.

Accelerated aging measurements were conducted in vacuum at 84°C on unsterilized HNS-IIA using the quartz spring balance apparatus. This data is shown in Figure 12. Excluding the cyclic variation of the data (due to vibrations, etc.), no significant change in weight occurs over the test period, 297 days (equivalent to 9.9 years at 66°C).

Additionally, a thermograph of a sample of unsterilized HNS-IIA after 183 days of accelerated aging (equivalent to 6.1 years) is shown in Figure 13. When compared with the initial thermograph, this figure shows no significant change in the thermal characteristics of the material.

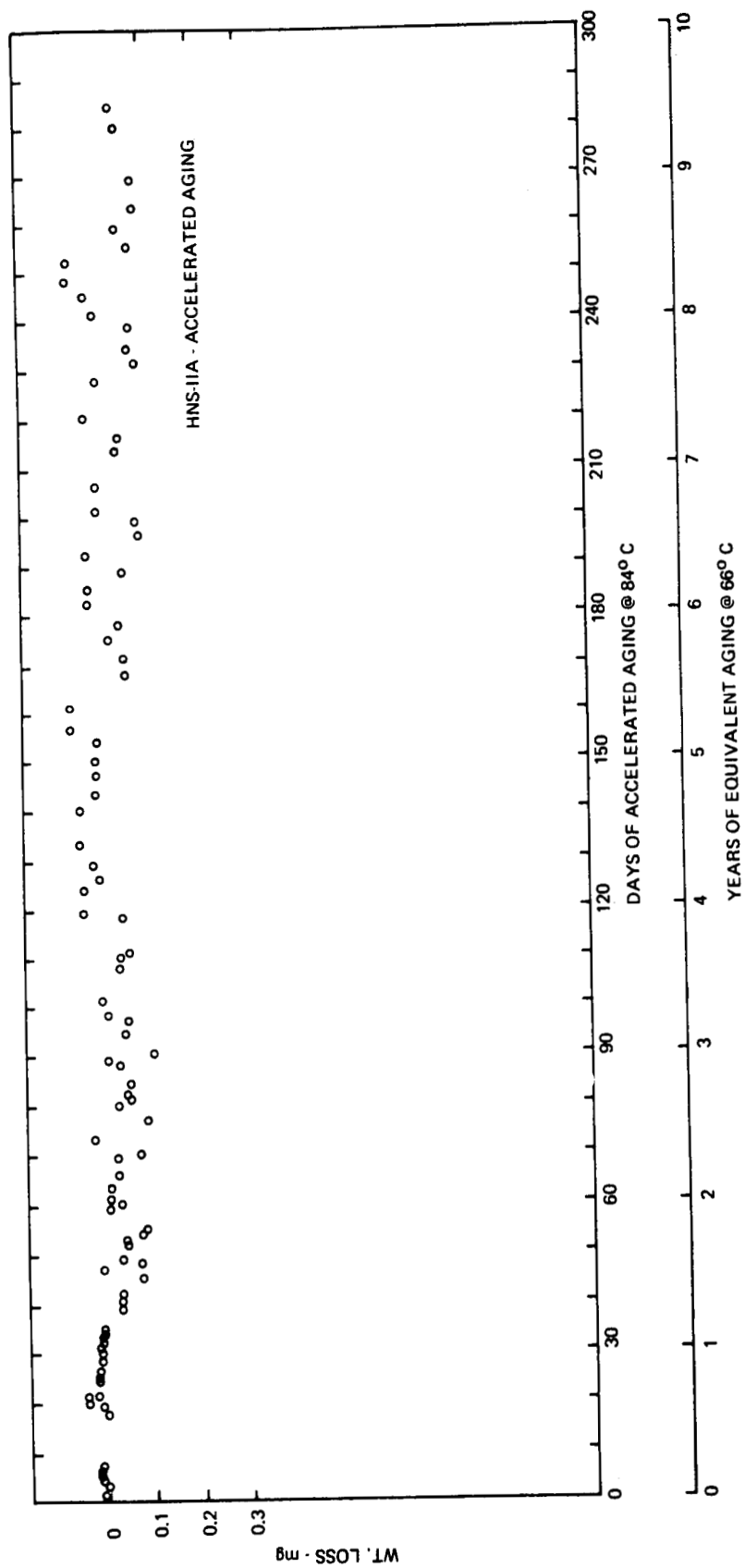


Figure 12. - Accelerated Aging Weight Loss for HNS IIA

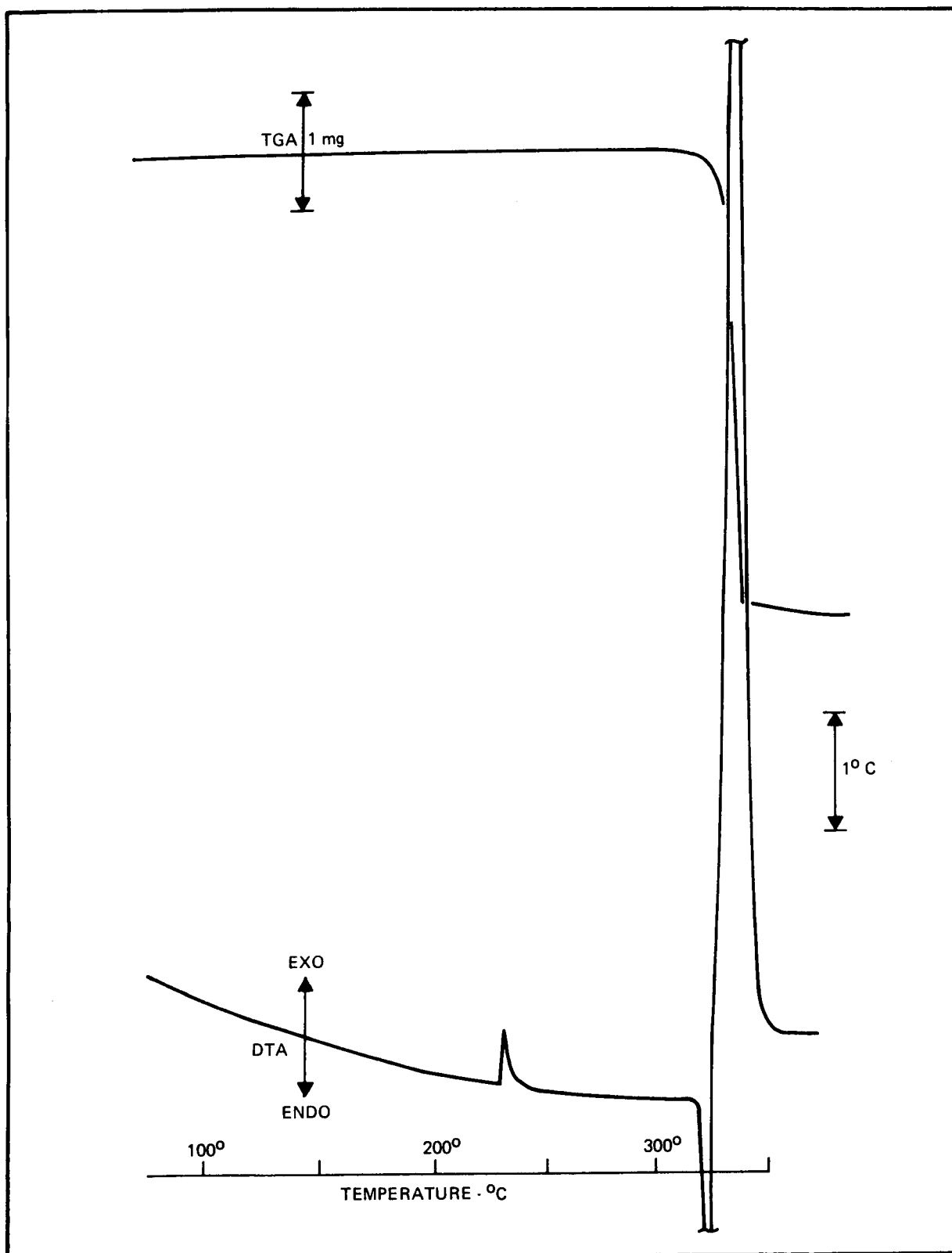


Figure 13. - Thermograph of HNS-IIA After 183 Days Accelerated Aging

Figure 14 is a thermograph of sterilized HNS-IIA after 94 days of accelerated aging equivalent to 3.1 years. Again, no significant change is observed.

Lead azide (PbN_6)

A very sensitive primary explosive, lead azide, can easily be detonated by impact, friction, heat or static discharge. Therefore, initially, dextrinated lead azide was selected as the test material because the dextrin reduces the initiation sensitivity of the PbN_6 thereby reducing the hazards involved in handling it.

Preliminary screening of the dextrinated PbN_6 produced the thermograph shown in Figure 15. Important features of this figure are the sharp exothermic decomposition peak occurring at 317°C with the accompanying precipitous weight loss in the TGA curve.

One sterilization cycle of 64 hours at 125°C caused the sharp exothermic decomposition peak to broaden and decrease in height, indicating that the rate of decomposition has decreased. The TGA curve showed a decrease in the rate of weight loss and the total weight loss was significantly smaller also.

Results following the second sterilization cycle (shown in Figure 16) are a further broadening and decrease in height of the decomposition peak. A further decrease in the rate and amount of weight lost is indicated by the TGA curve. These results indicate a change has occurred in the dextrinated PbN_6 as a result of sterilization.

Scanning electron micrographs taken of dextrinated PbN_6 before and after two sterilization cycles are shown in Figures 17 and 18. Figure 17 shows the material in the "as received" condition at 2000X magnification; Figure 18 shows a sample of the material at the same magnification after two sterilization cycles. From comparison of these micrographs, no change is apparent in the morphology of the dextrinated lead azide as a result of sterilization.

For measurement of the sublimation rate of dextrinated PbN_6 , temperatures from 120°C to 180°C were selected for testing. The data for the weight loss as a function of time at various temperatures are shown in Figure 19. At 120° and 140°C , the rates of weight loss remain relatively constant. However, at 160° and 180°C , the initial rates of weight loss decrease markedly after approximately 40 hrs. then increase again after approximately 110 hrs. Prior experience indicates that pure PbN_6 would not

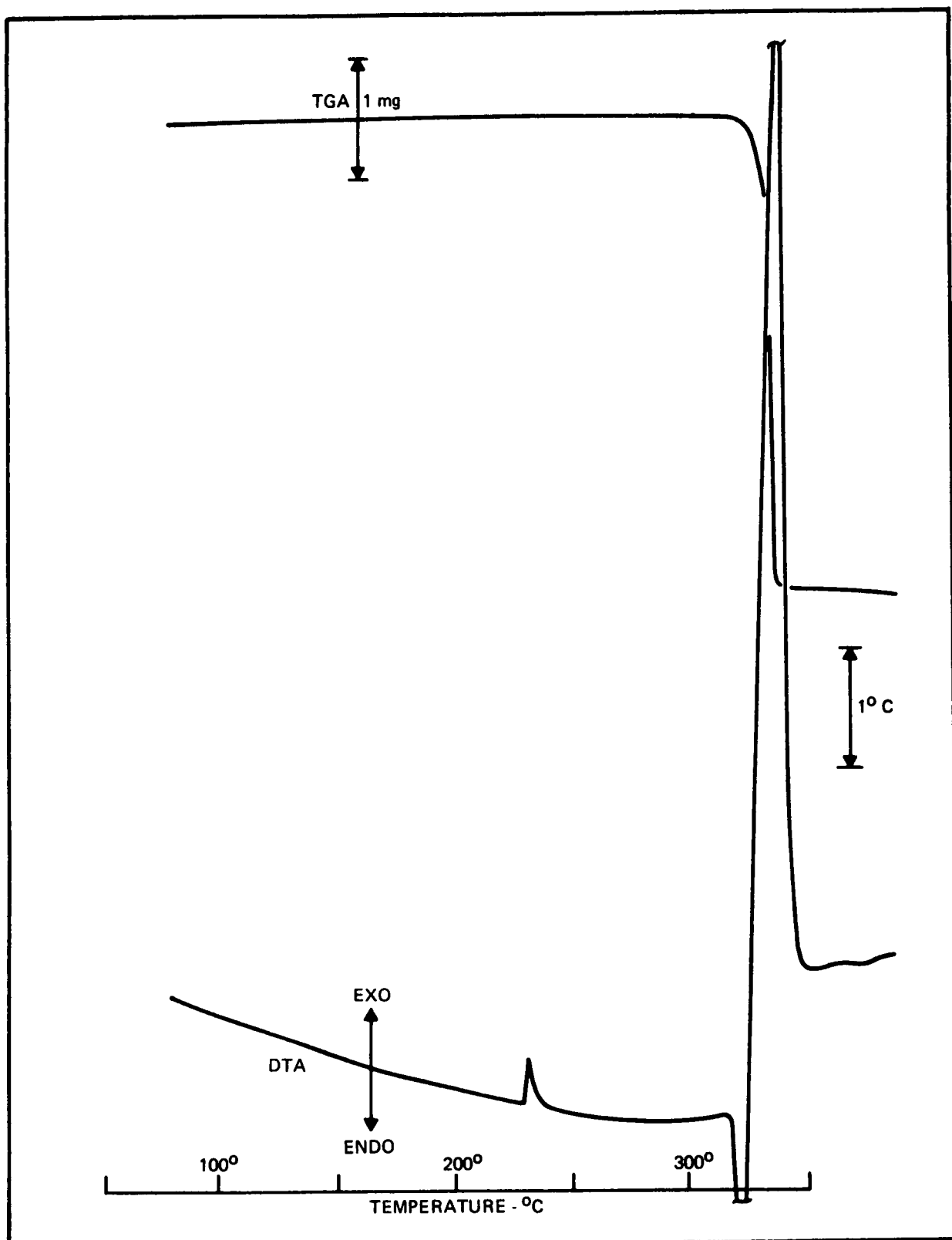


Figure 14. - Thermograph of Sterilized HNS-IIA After 94 Days Accelerated Aging

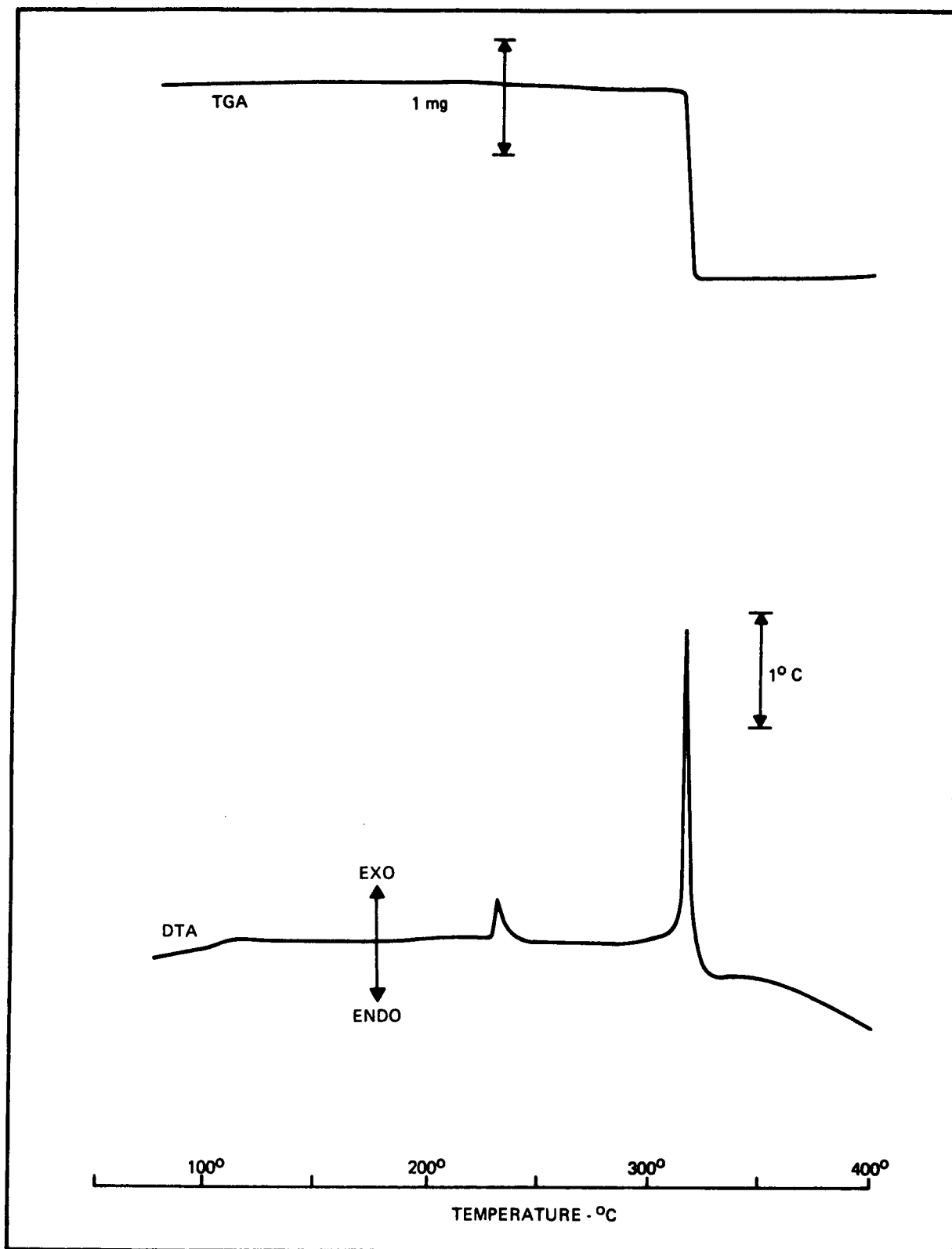


Figure 15. - Initial Thermograph for Dextrinated PbN_6

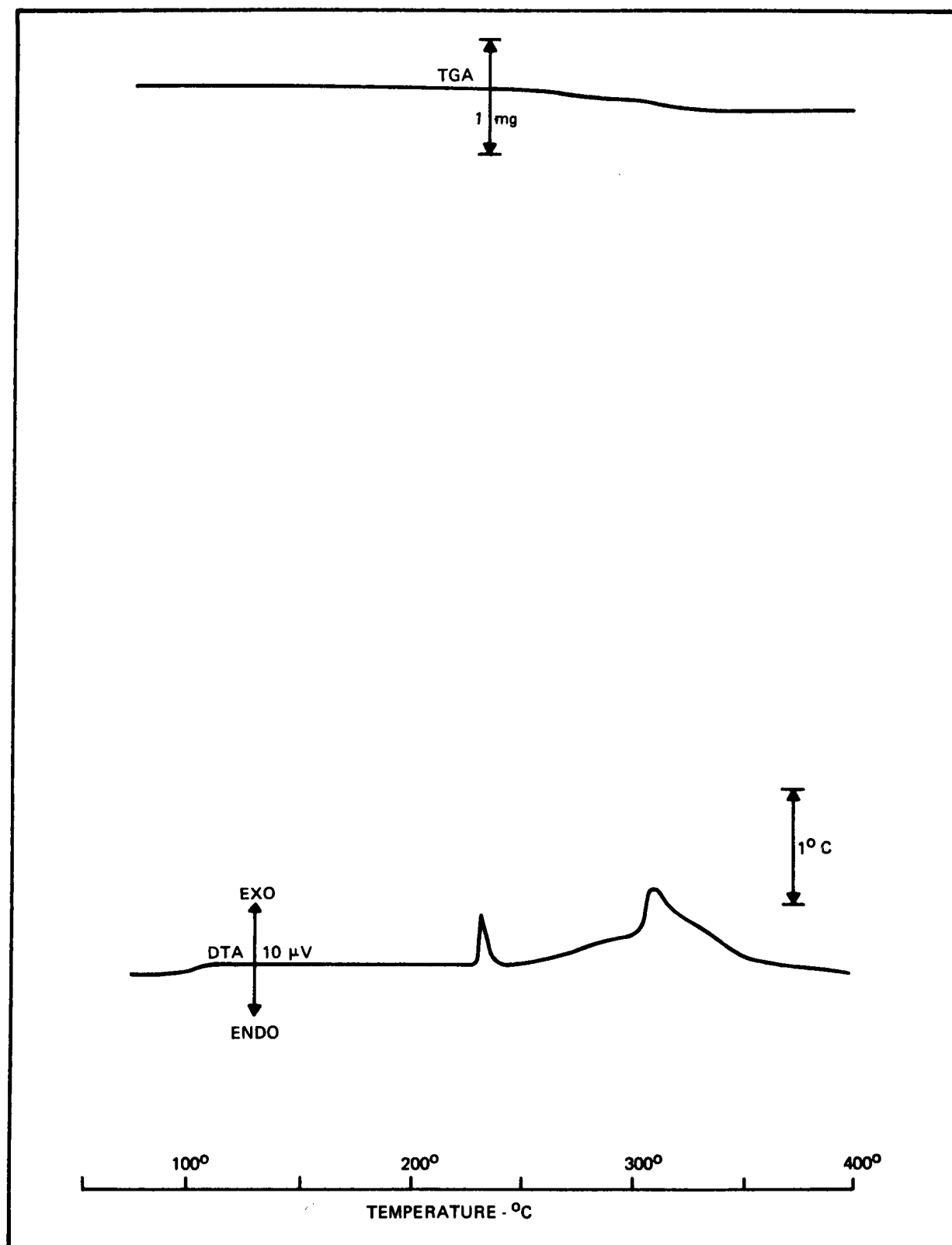


Figure 16. - Thermograph of Dextrinated PbN_6 After Two Sterilization Cycles

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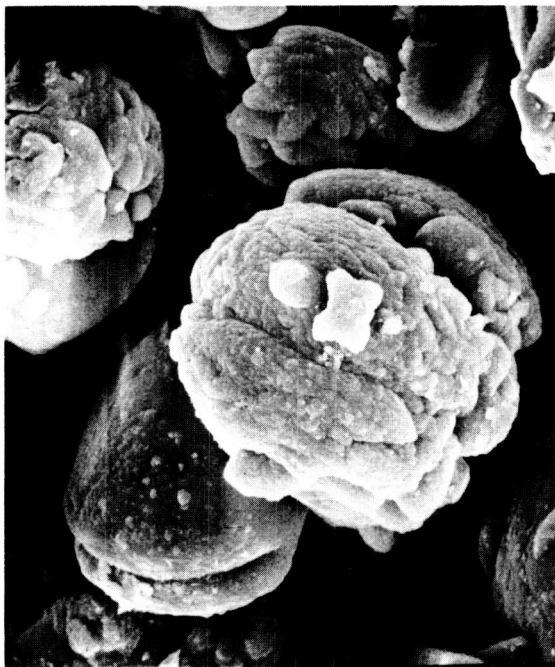


Figure 17. - Dext. PbN₆—Before Sterilization (200X)



Figure 18. - Dext. PbN₆—After Sterilization (2X, 64 hr, 125° C) (2000X)

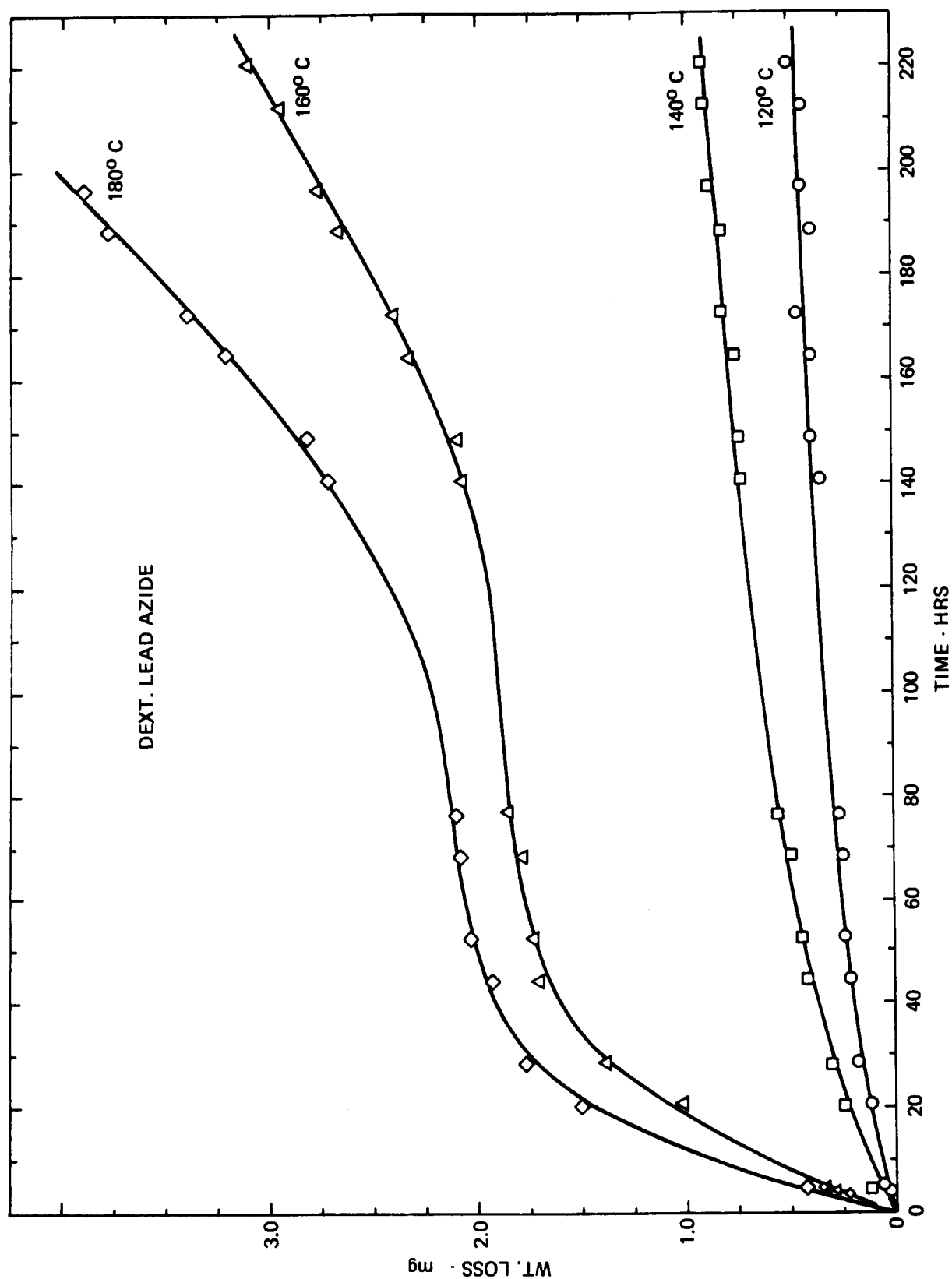


Figure 19.- Sublimation Plot for Dextrinated PbN_6

exhibit this stepwise decomposition and should be relatively stable at these temperatures. Therefore, it is probable that the dextrin is decomposing, possibly by a dehydration reaction which could proceed in a stepwise fashion.

Weight loss rates and sublimation rates calculated from the data shown in Figure 19 are given in Table III below. The rates at the higher two temperatures (160° and 180°C) are based on the data taken during the first 20 hours of testing.

TABLE III. - SUBLIMATION RESULTS FOR DEXTRINATED PbN_6

Temperature °C	Wt. Loss Rate mg/hr	Sublimation Rate gm/cm ² /sec
120	1.43×10^{-3}	6.02×10^{-10}
140	2.0×10^{-3}	7.42×10^{-10}
160	5.0×10^{-2} (a)	2.10×10^{-8} (a)
180	7.5×10^{-2} (a)	2.78×10^{-8} (a)

(a) Based on data taken during the first 20 hours of testing.

Isothermal decomposition measurements were made on dextrinated PbN_6 in the open-to-atmosphere (OA) test environment over the temperature range of 150°C to 200°C. These data were analyzed in a manner similar to that shown for HNS, and the results are given in Table IV. Listed in the table are the measured activation energy (E_a), the calculated rate constant at 66°C (k), the accelerated-aging rate constant (K_A) required for one months aging to equal one year at 66°C, and the calculated accelerated-aging temperature (T_A) necessary to obtain k_A .

TABLE IV. - ISOTHERMAL DECOMPOSITION DATA FOR DEXT. PbN_6

Conditions	Activation Energy Kcal/mole	k @ 66°C sec ⁻¹	K_A One Year @ 66°C	T_A Accel. Aging Temp. °C
Open Air	21.7	2.28×10^{-8}	2.7×10^{-7}	94.7

At this point, based upon the results obtained, the decision was made to change from dextrinated lead azide to pure lead azide. The dextrinated material did not appear capable of withstanding sterilization and the activation energy measured was significantly lower than the value for pure lead azide in the literature. It was decided that pure lead azide would be prepared as described under the Materials section and tested for sterilization and accelerated-aging measurements.

Results of the sterilization test of pure lead azide are shown in Figures 20 and 21. Figure 20 is the thermograph for pure PbN_6 before sterilization; Figure 27 is the result following two sterilization cycles. Comparison of the thermographs shows that the only change is an upward shift of the main decomposition exotherm peak temperature from 302° to 328°C . This would indicate a slightly greater degree of stability, but the rate of decomposition and weight loss did not change.

SEM photographs before and after sterilization are shown by Figures 22 and 23, respectively. These micrographs indicate no apparent change in the morphology of pure PbN_6 due to sterilization.

Since pure PbN_6 has been the subject of considerable research, literature values of the rate constant and activation energy were used to calculate the accelerated-aging parameters, thus minimizing the delay in beginning the accelerated-aging measurements of this alternate material. The values obtained are:

	<u>Source</u>
Activation energy ~36 kcal/mole	Evans, Yoffe and Gray (22)
	Hutchinson, et al. (23)
	Griffiths and Grocock (24)
	Jach (25)
	Pai Verneker and Maycock (26)
Rate Constant $5.95 \times 10^{-6} \text{ sec}^{-1}$ @ 210°C	
	Kleinberg and Stein (27)

Based upon these values, the values in Table V were calculated for the aging parameters:

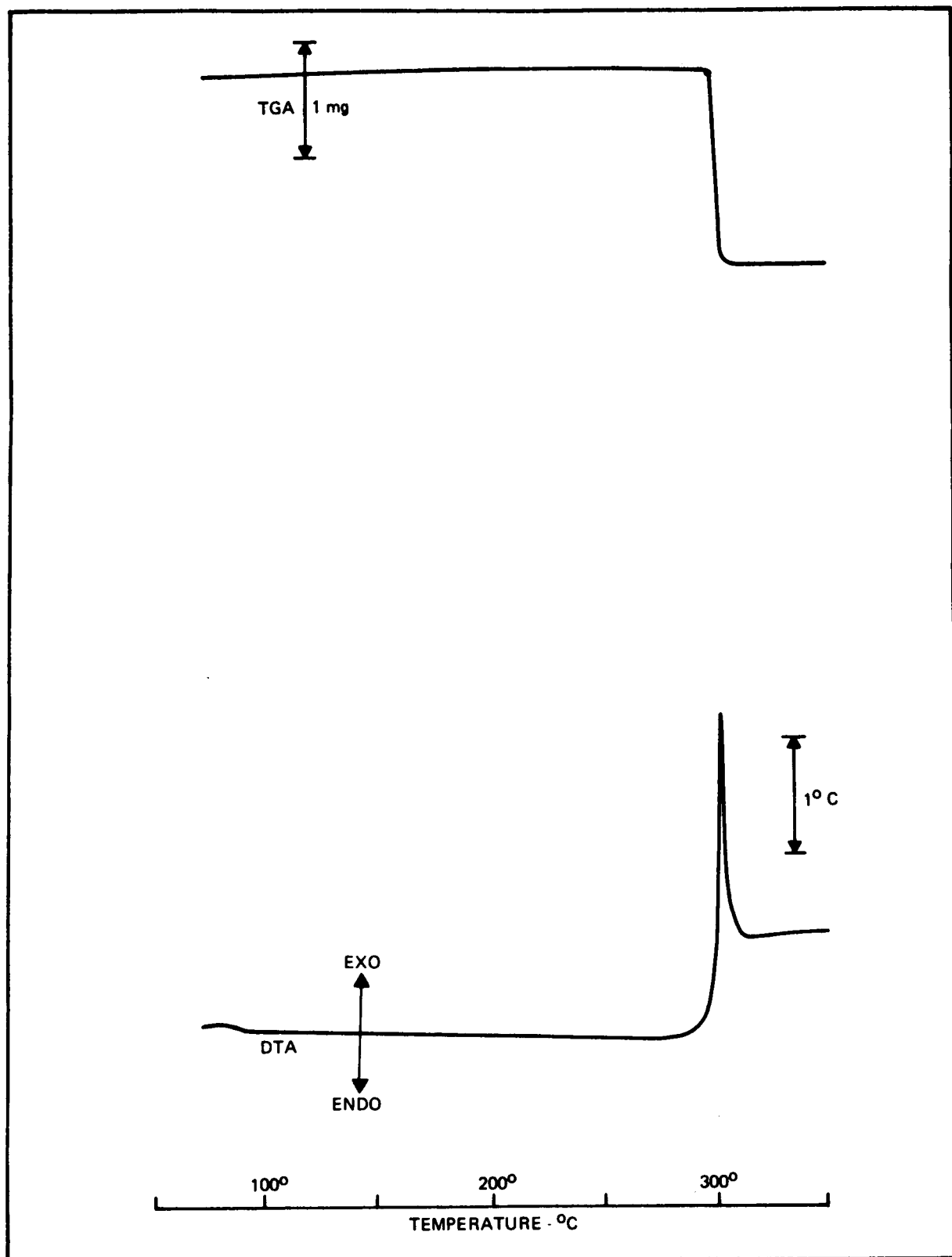


Figure 20. - Initial Thermograph for Pure PbN_6

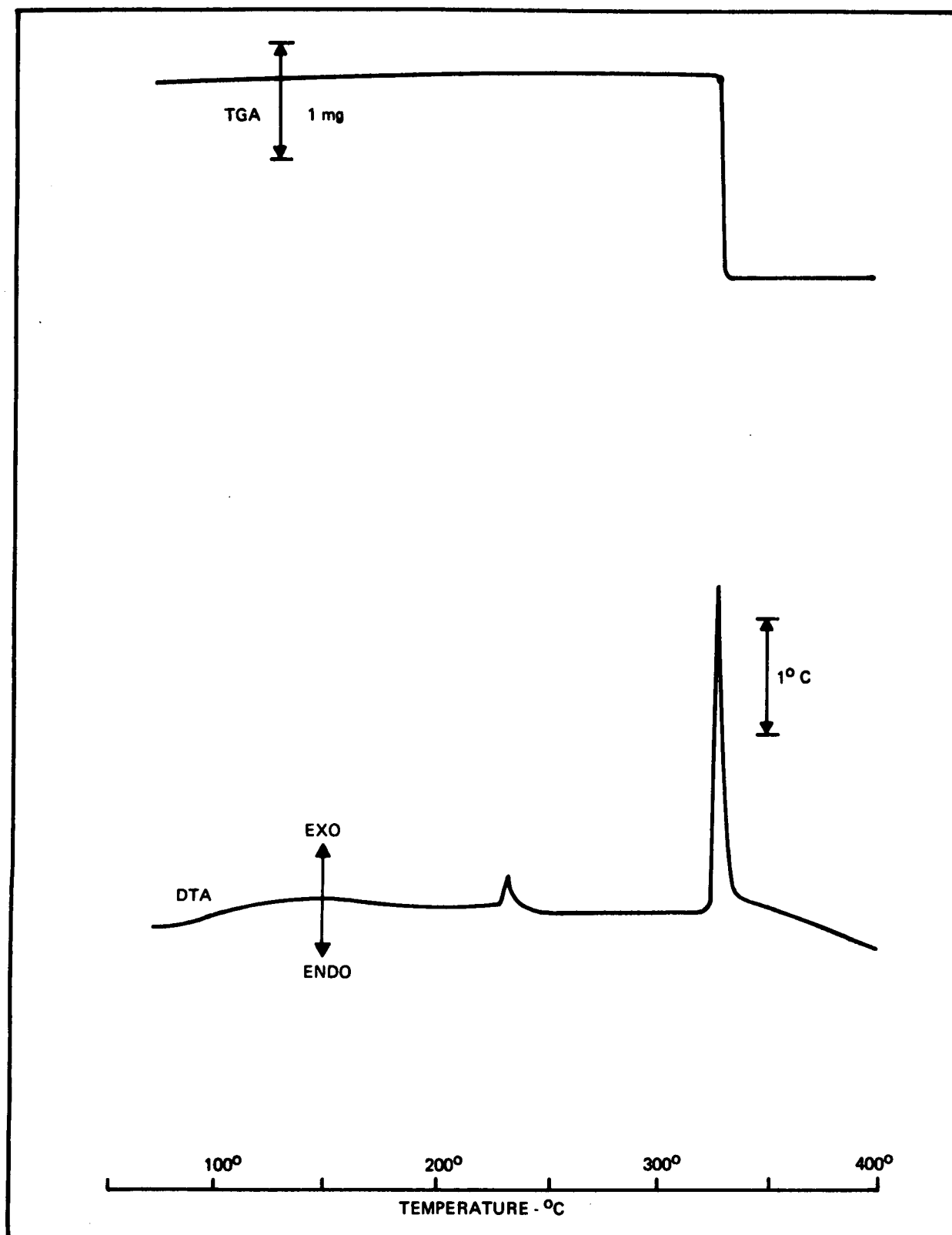


Figure 21. - Thermograph of Pure PbN_6 After Two Sterilization Cycles

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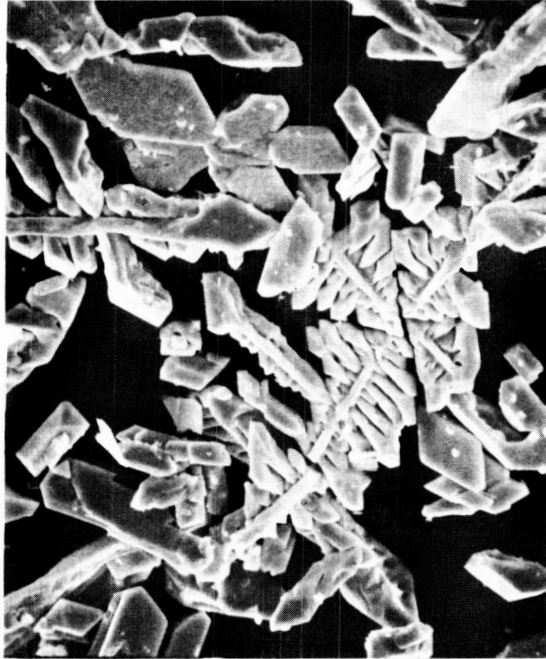


Figure 22. - Pure PbN_6 —Before Sterilization (600X)



Figure 23. - Pure PbN_6 —After Sterilization (2X, 64 hr, 125° C) (600X)

TABLE V. - ACCELERATED AGING PARAMETERS FOR PURE PbN_6

Conditions	Activation Energy Kcal/ mole	k @ 66°C sec ⁻¹	^a One Year @ 66°C	Ta Accel. Aging Temp °C
Closed Vol.	36	3.32×10^{-13}	1.05×10^{-5}	81.9°

Accelerated aging of the pure lead azide was performed at 84°C in vacuum. Data obtained from the quartz spring balance for the accelerated aging of unsterilized pure PbN_6 are presented in Figure 24. Unfortunately, this balance seemed to be more sensitive to external vibrations, etc. than the other balances and exhibited a fairly large cyclic variation. This would tend to mask very small weight losses, however, the mean value can be used to follow the total weight loss. Over the 228 days (equivalent to 7.6 years at 66°C) duration of the test pure PbN_6 lost ~0.15 mg (0.44%).

Thermal analysis of a sample of PbN_6 after 183 days of accelerated aging (equivalent to 6.1 years) shows no significant change in the thermograph (Figure 25) after this period.

For sterilized pure PbN_6 , however, the results were different. The thermograph in Figure 26 was obtained after 66 days of accelerated aging (equivalent to 2.2 years). Examination of the DTA curve indicates that the main decomposition exotherm has decreased in size and broadened. These changes are reflected in the TGA curve, also, in both the amount and rate of weight loss.

It is noteworthy that unsterilized PbN_6 is capable of withstanding accelerated aging for almost three times as long as sterilized PbN_6 . Possibly the sterilization process, in the presence of air, promotes the formation of basic lead azide and/or decomposition nuclei which serve as initiation sites for further decomposition.

Potassium dinitrobenzofuroxan (KDNEBF)

The initial thermograph obtained during the preliminary screening of KDNEBF is shown in Figure 27. The main decomposition exotherm peak for this material occurred at 203°C.

Following two sterilization cycles, the results in Figure 28 were obtained. The only change noted is the shift of the main decomposition peak to 177°C.

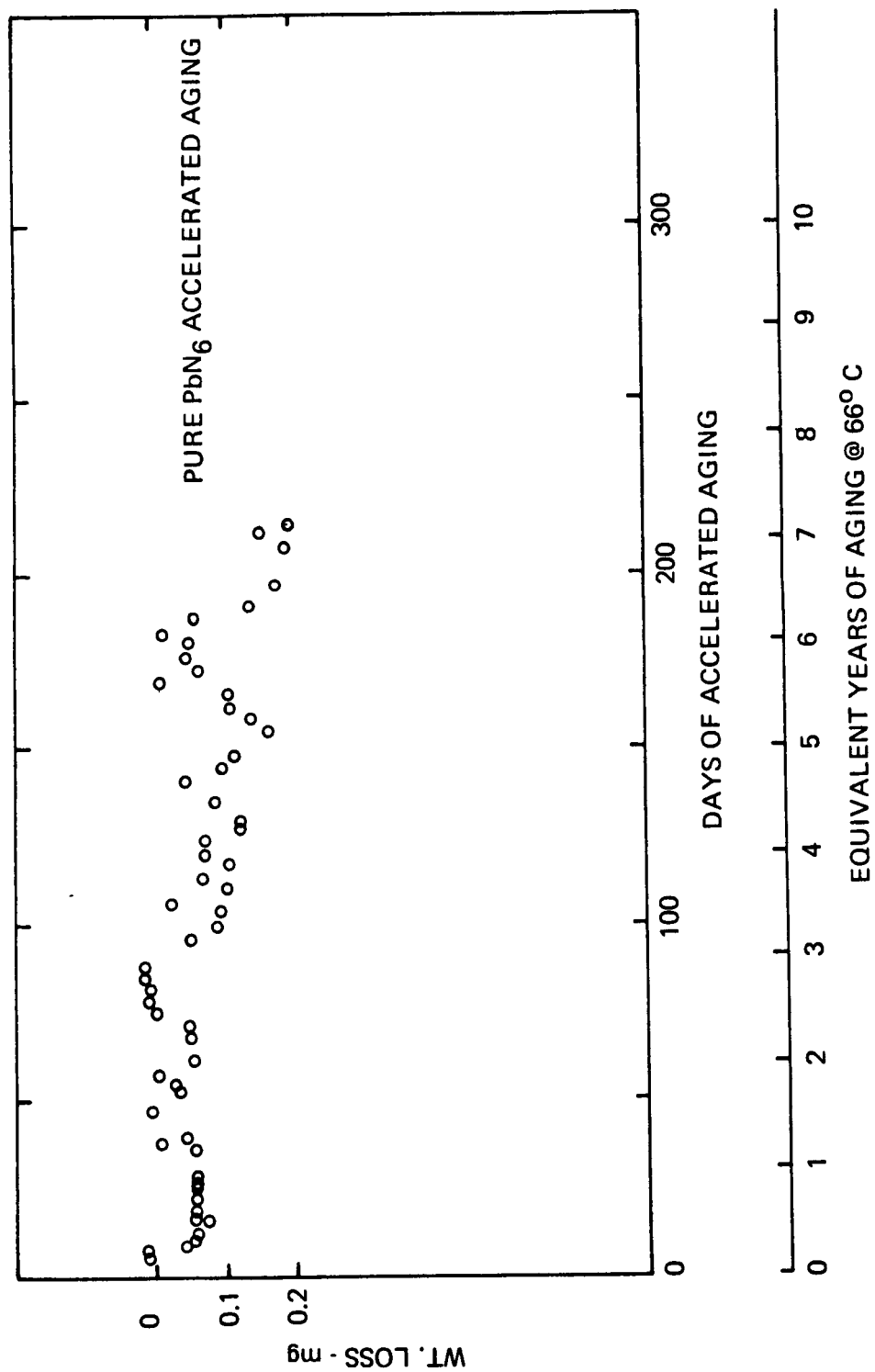


Figure 24. - Accelerated Aging Weight Loss for Pure PbN₆

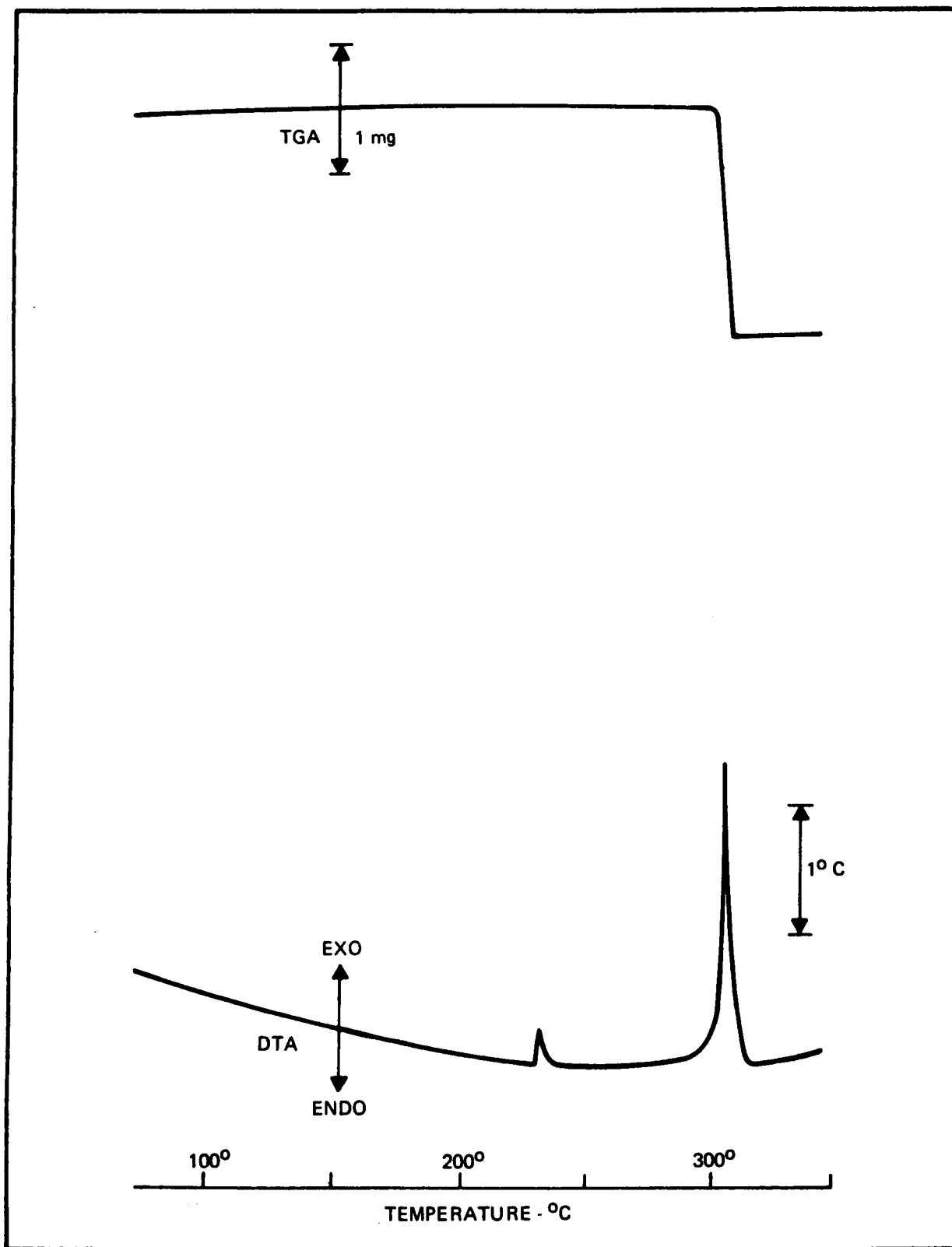


Figure 25. - Thermograph of Pure PbN_6 After 183 Days Accelerated Aging

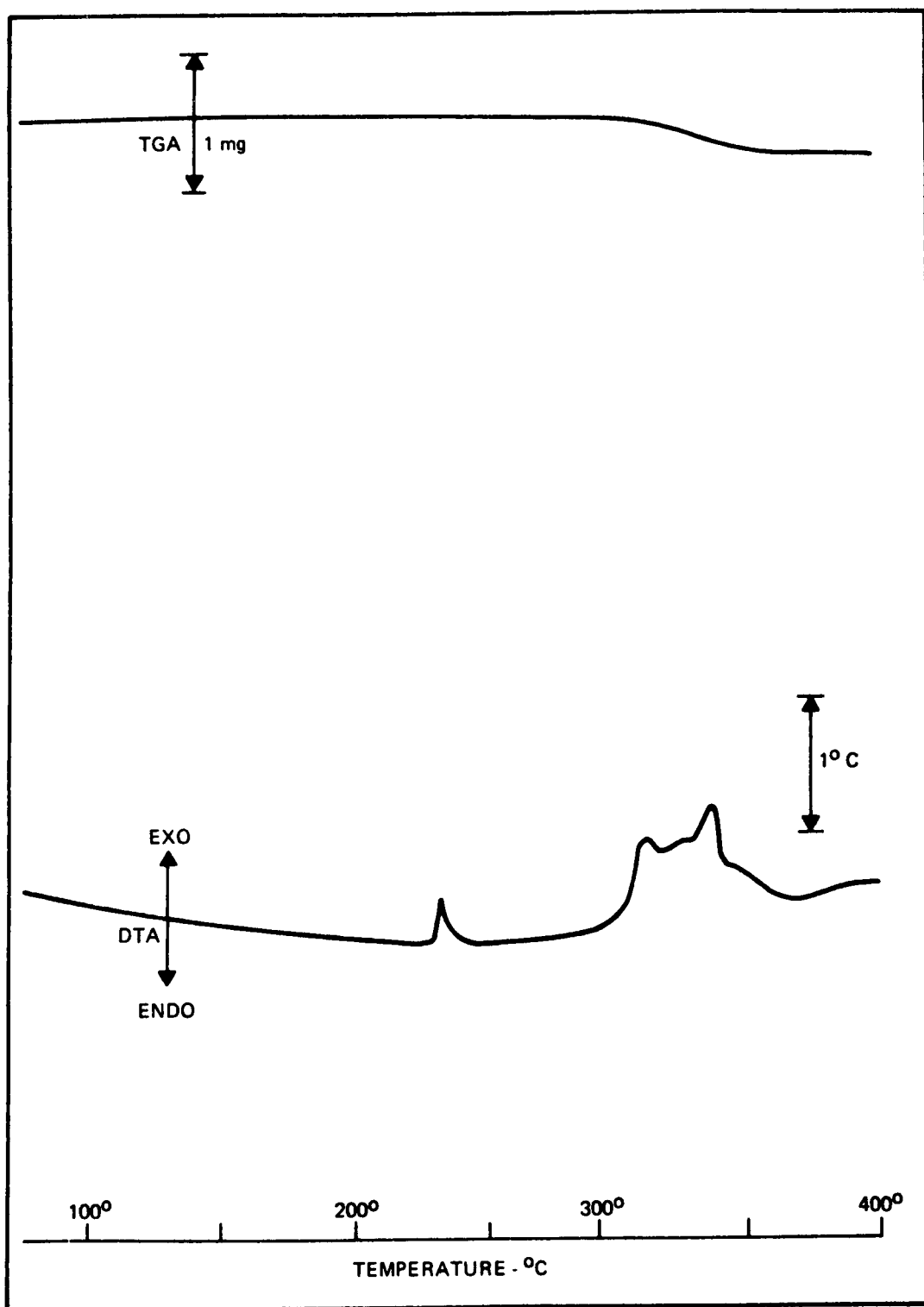


Figure 26. - Thermograph of Sterilized Pure PbN_6 After 66 Days Accelerated Aging

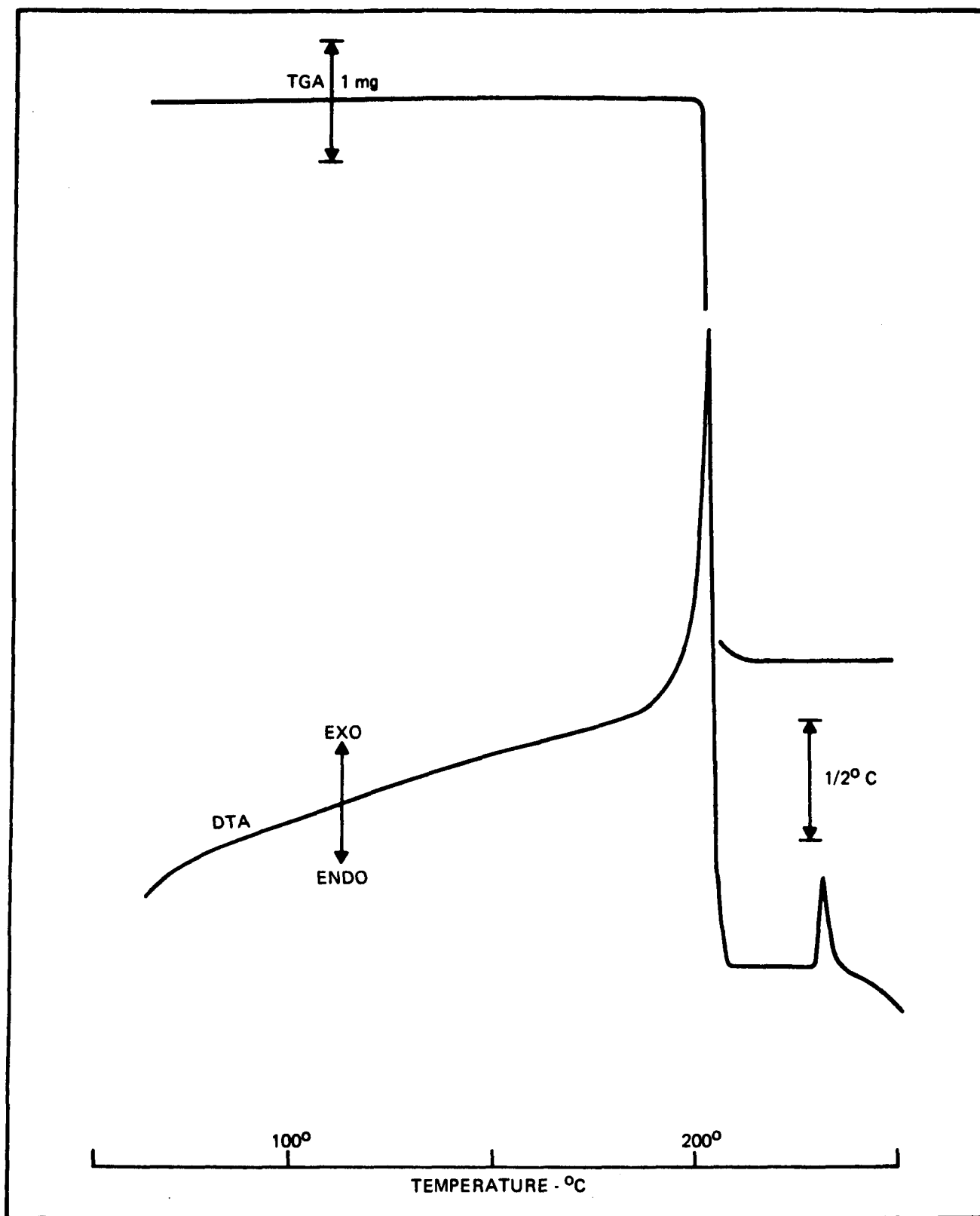


Figure 27. - Initial Thermograph for KDNBF

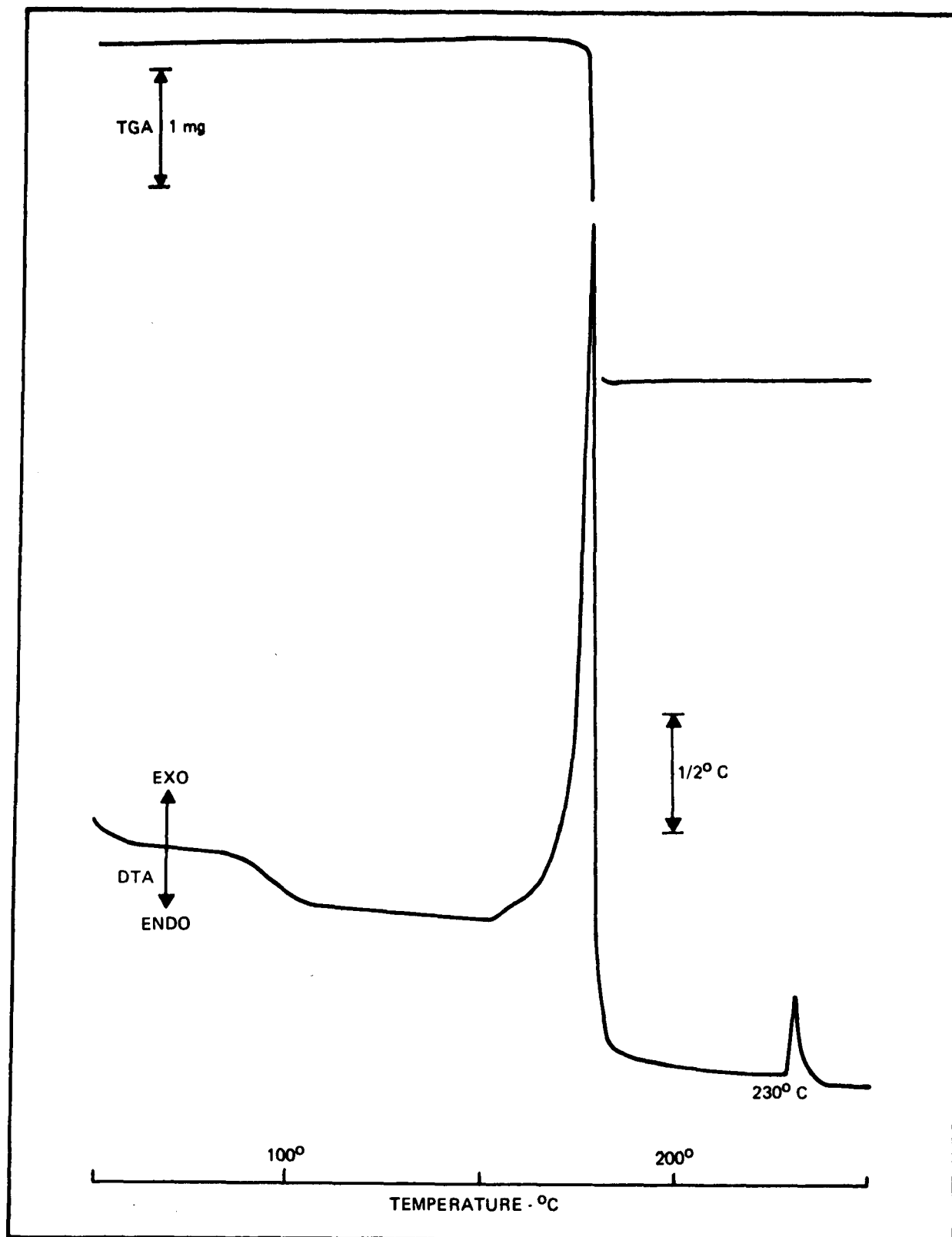


Figure 28. - Thermograph of KDNBF After Two Sterilization Cycles

SEM photographs taken before and after two sterilization cycles are shown in Figures 29 and 30, respectively. Examination of these figures indicates no change in the morphology of the material as a result of sterilization.

Sublimation measurements were not conducted on KDNBF because they were not within the scope of the contract.

As shown by the initial thermograph, this material detonates at approximately 200°C, therefore to be realistic within the mission restraints, isothermal decomposition studies were conducted between 90° and 150°, for all four environmental mission possibilities. The choice of this temperature range was also dictated by the requirement to have decomposition studies of the same phenomena which would be expected at 66°C.

The data obtained for these decompositions present a paradox in that they fall into one of two classes: (1) the time required for a given fractional decomposition as a function of temperature is relatively constant, implying a very small activation energy or that the weight loss phenomena is relatively independent of temperature and (2) the time required for a given fractional decomposition increases. For a pure, unsolvated, material these effects would not occur. Thus the implication is that the KDNBF may contain occluded solvent introduced in the manufacturing process. (However, a supplemental mass spectrometric analysis failed to detect the presence of any occluded solvent.)

Only under the continuously pumped vacuum condition could usable data be obtained and these are given in Table VI. Parameters for the other test conditions could not be obtained due to the inconsistencies in the data.

TABLE VI. - ISOTHERMAL DECOMPOSITION RESULTS FOR KDNBF

Conditions	Activation Energy Kcal/mole	k @ 66°C Sec ⁻¹	One Year @66°C	Ta Accel. Aging Temp. °C
Cont. Pumped Vac.	30.2	4.37 x 10 ⁻⁸	-	86.1°

Results of the accelerated aging of unsterilized KDNBF in the quartz spring balance apparatus are shown in Figure 31. This material exhibited a weight loss from the beginning of the test. Over a 255 day test period (equivalent to 8.5 years) KDNBF lost 0.55 mg (1.32%).

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Figure 29. - KDNBF—Before Sterilization (600X)



Figure 30. - KDNBF—After Sterilization (2X, 64 hr, 125° C) (600X)

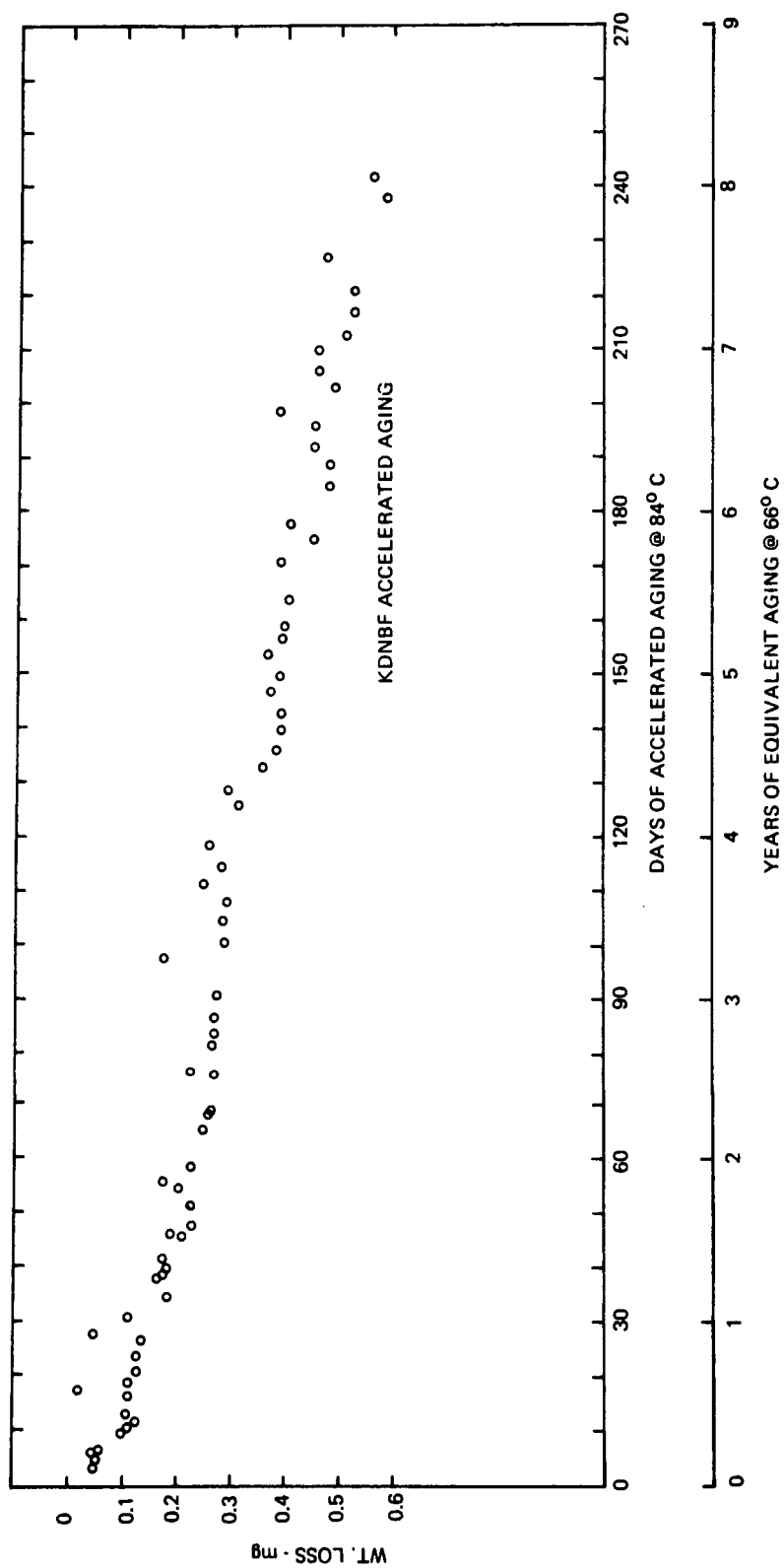


Figure 31. - Accelerated Aging Weight Loss for KDNBF

Further accelerated-aging data are shown in Figure 32, a thermograph for unsterilized KDNBF after 183 days of accelerated aging (equivalent to 6.1 years). It shows no significant change from the initial thermograph.

Zirconium - potassium perchlorate pyrotechnic propellant (Zr/KClO₄)

Results of the preliminary screening test of Zr/KClO₄ are shown in Figure 33. The main features of this figure are: the melting of the tin reference at 230°C, the phase-change endotherm of KClO₄ at 311°C, and the main decomposition exotherm at 411°C.

Sterilization of the Zr/KClO₄ produced no significant change in thermal characteristics of the material. The results following two sterilization cycles are shown in Figure 34.

Additionally, SEM micrographs show no change in the morphology of the material as a result of sterilization. The material before sterilization is shown in Figure 35; Figure 36 shows the results following two sterilization cycles.

Sublimation measurements were conducted on Zr/KClO₄ in vacuum over the temperature range of 100° to 180°C. No measurable weight loss was observed for Zr/KClO₄ over a test period of 269 hours.

Results of the isothermal decomposition measurements on Zr/KClO₄ over the temperature range of 250° to 300°C are summarized in Table VII.

TABLE VII. - ISOTHERMAL DECOMPOSITION RESULTS FOR Zr/KClO₄

Conditions	Activation Energy Kcal/ mole	k @ 66°C Sec ⁻¹	^a One Year @ 66°C	T _a Accel. Aging Temp °C
Cont. Pumped Vac.	17.5	1.01 x 10 ⁻⁹	2.19 x 10 ⁻²	102.2°
Closed Vol. Vac.	29.9	1.21 x 10 ⁻¹²	3.82 x 10 ⁻⁵	86.5°
Open Air	17.2	2.97 x 10 ⁻¹⁰	9.36 x 10 ⁻³	94°
Closed Vol. Air	2.8	2.80 x 10 ⁻⁵	-	-

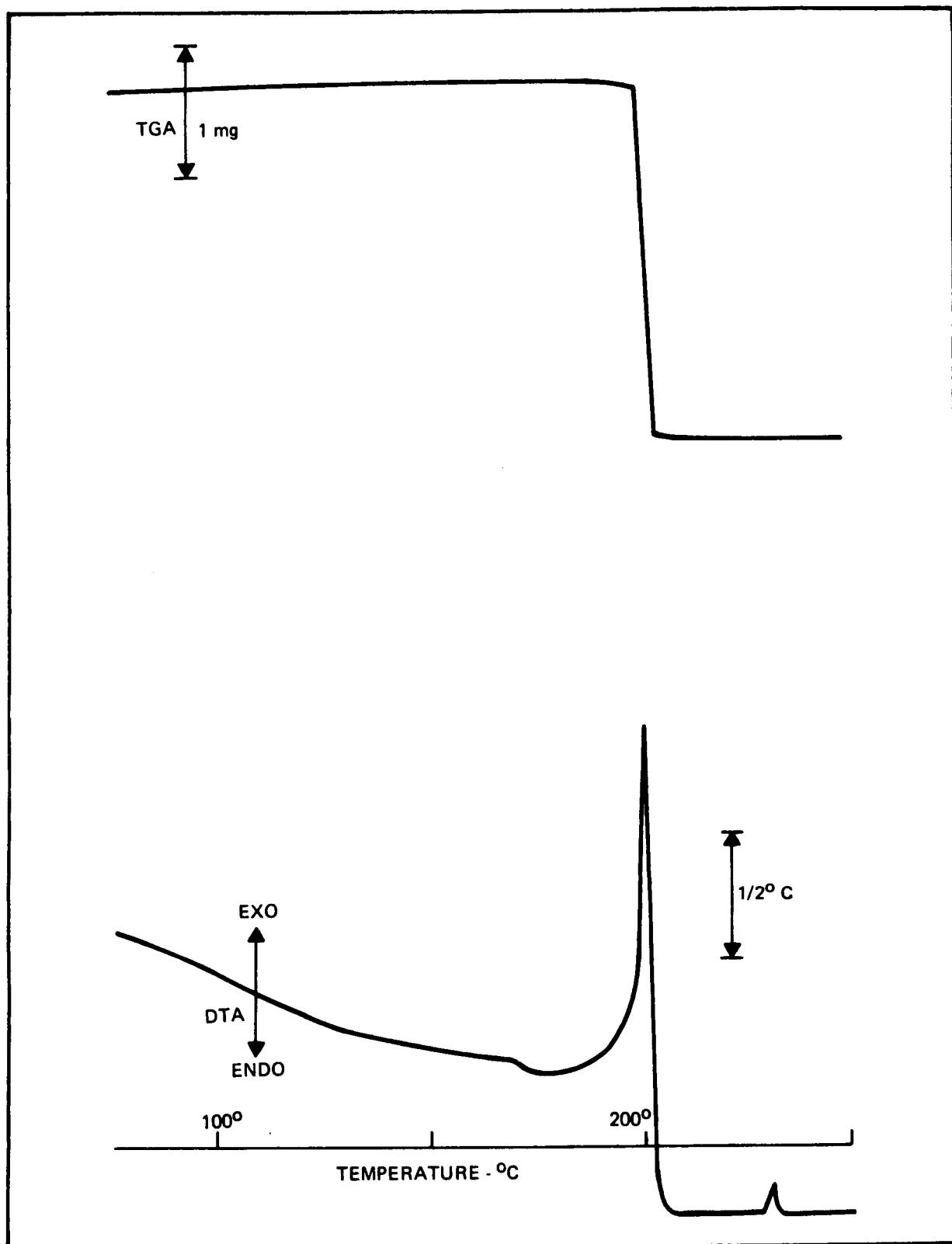


Figure 32. - Thermograph of KDNBF After 183 Days Accelerated Aging

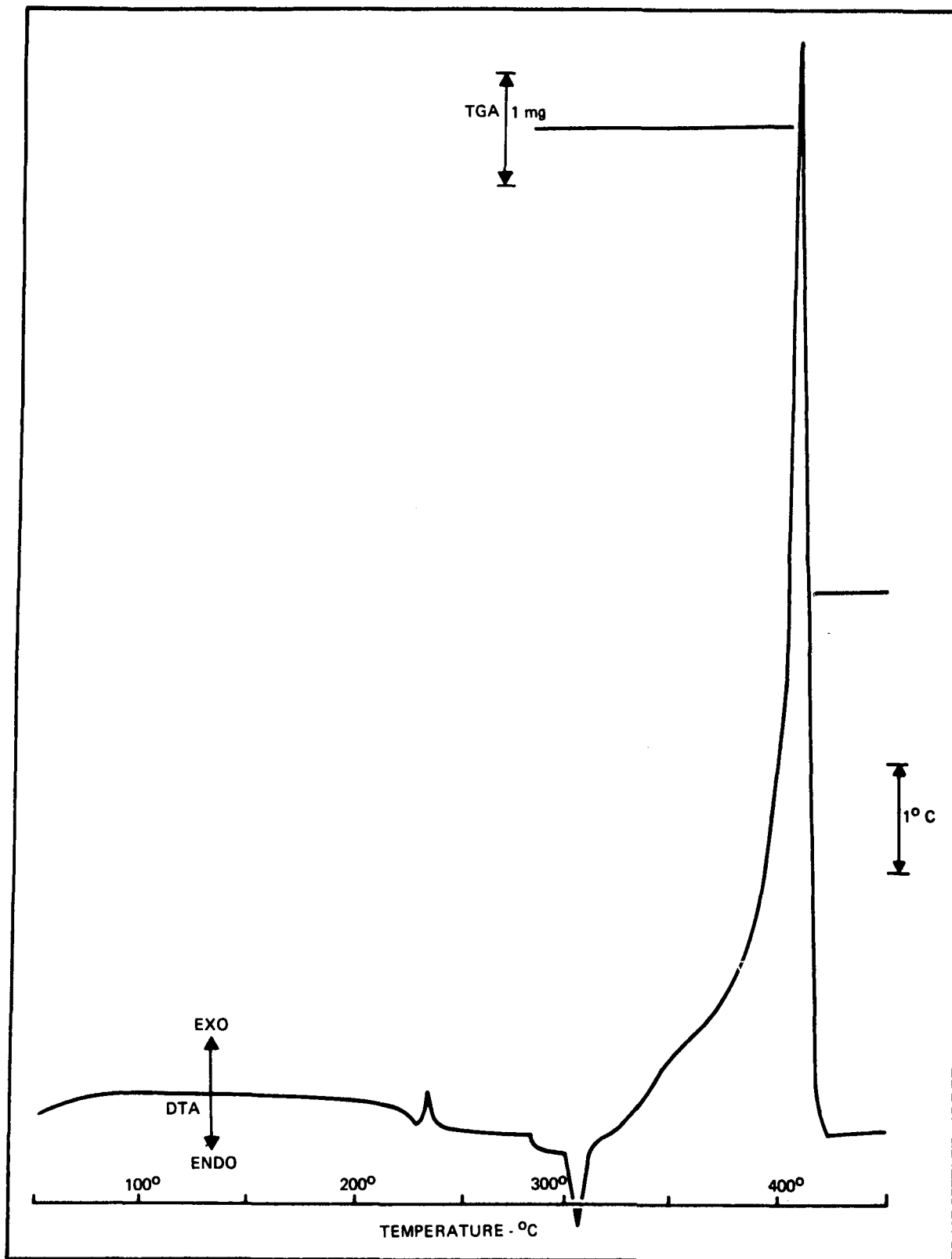


Figure 33. - Initial Thermograph for Zr/KClO₄

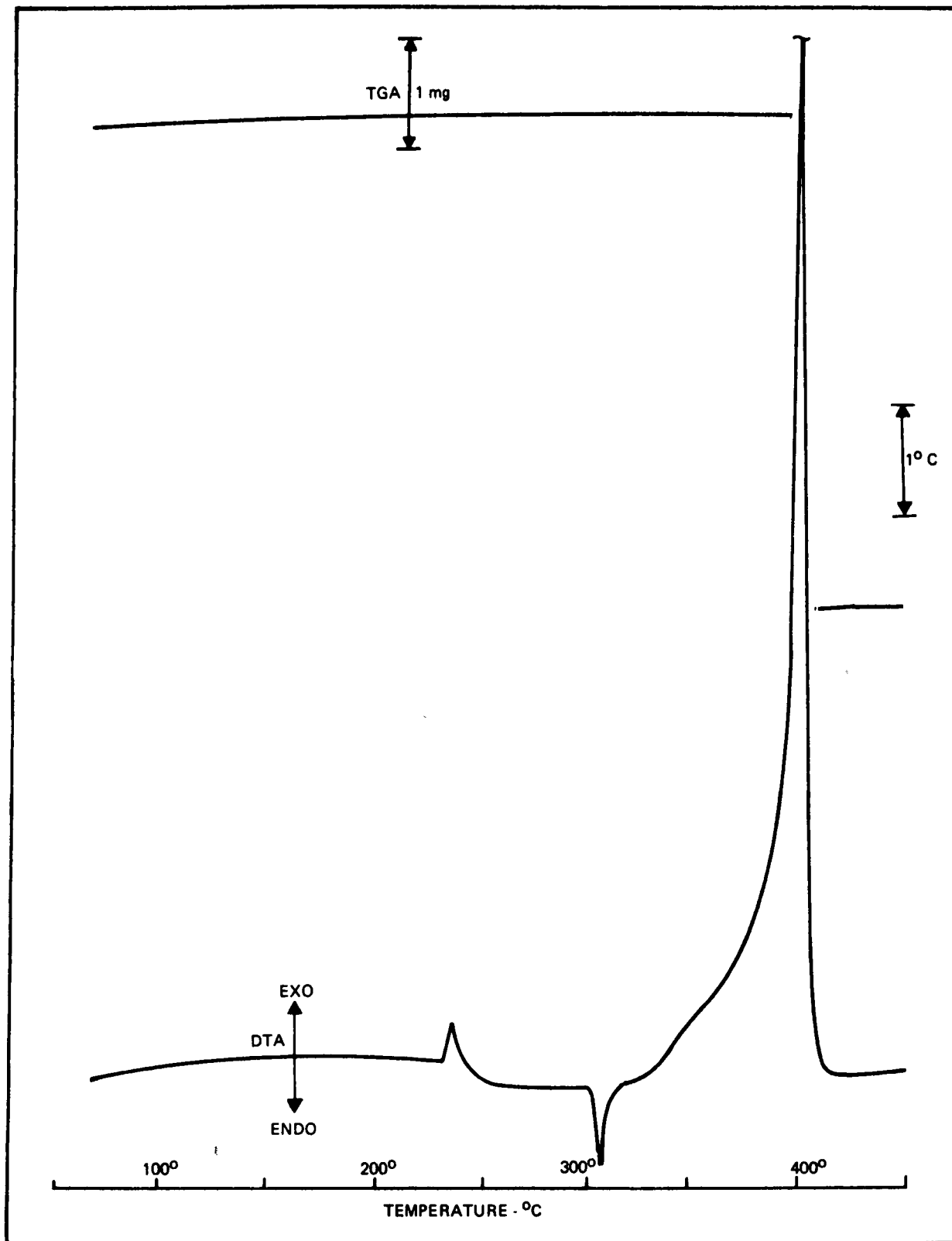


Figure 34. - Thermograph of Zr/KClO_4 After Two Sterilization Cycles

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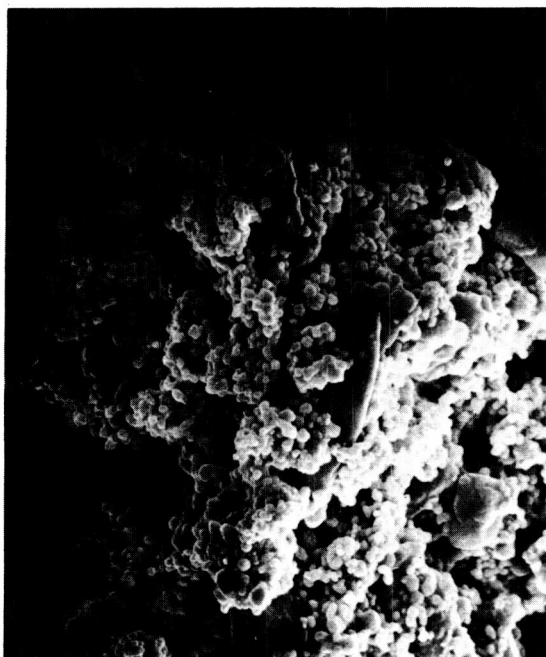


Figure 35. - Zr/KClO_4 —Before Sterilization (1000X)

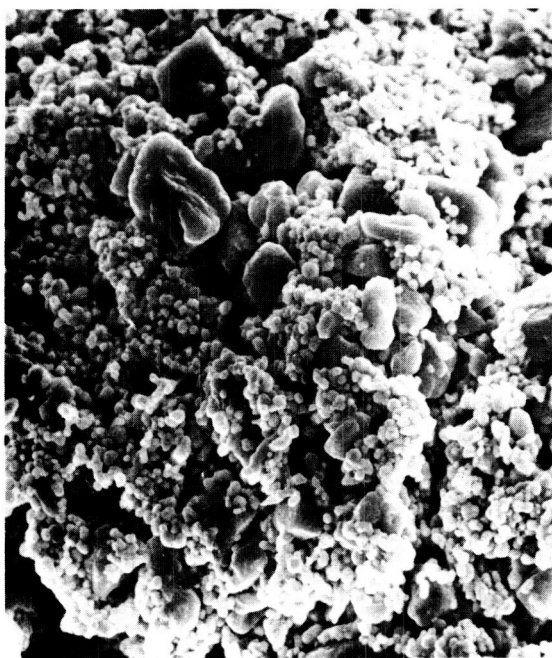


Figure 36. - Zr/KClO_4 —After Sterilization (2X, 64 hr, 120°C) (1000X)

Based upon the rate constant at 66°C measured under closed volume air test conditions, the α for one year would be greater than one, which is not possible. It appears that the true decomposition is being masked by side effects or complex interactions under these conditions.

Data for the accelerated aging of unsterilized Zr/KClO_4 in the quartz spring balance apparatus is shown in Figure 37. No measurable weight loss was observed during the test period (251 days, equivalent to 8.4 years at 66°C).

Following 183 days of accelerated aging (equivalent to 6.1 years) for unsterilized Zr/KClO_4 , the thermograph in Figure 38 was made. It indicates no significant changes in the thermal properties of the material.

Additionally, a thermograph (Figure 39) of sterilized Zr/KClO_4 was prepared after 94 days of accelerated aging (equivalent to 3.1 years). The figure shows a change has taken place in the material. The exothermic peak at 403°C has decreased in size and a new exothermic peak appears at 486°C . This change was not apparent after 39 days of accelerated aging for the sterilized material. It is possible that some oxidation occurs during sterilization creating initiating sites which serve to promote the degradation during accelerated aging (See discussion under B/KClO_4 .)

Boron - potassium perchlorate (B/KClO_4)

Preliminary screening test of B/KClO_4 produces the thermograph shown in Figure 40. Major features of the figure are the tin reference peak at 230°C , the phase change of KClO_4 at 311°C , and the main decomposition peak exotherm at 381°C .

Significant changes were noted in the thermographs following sterilization. The results following two sterilization are shown in Figure 41. The decomposition exotherm at 381°C has become much smaller and broader with a new large decomposition exotherm appearing at 461°C . The results obtained after one sterilization cycle were similar to those after two cycles except for minor changes in the exotherm temperatures. It appears that sterilization has drastically changed the chemical integrity of the B/KClO_4 propellant. Comparison of the areas under the curves suggests that the sterilized propellant is more exothermic - this is an artifact of the measuring technique and will be discussed later. A compilation of these thermal events for sterilized and unsterilized propellant is presented in Table VIII.

Since during sterilization no measure of any weight change in the sample was recorded, the experiment was repeated with samples in the Mettler Thermoanalyzer in air for 64 hours at 125°C so that a direct measure of weight changes could be made. To account for possible reactions with oxygen in the air the experiment was repeated in a flowing nitrogen atmosphere. The data show in both cases substantial weight loss during the sterilization cycles. Typical values are listed in Table IX.

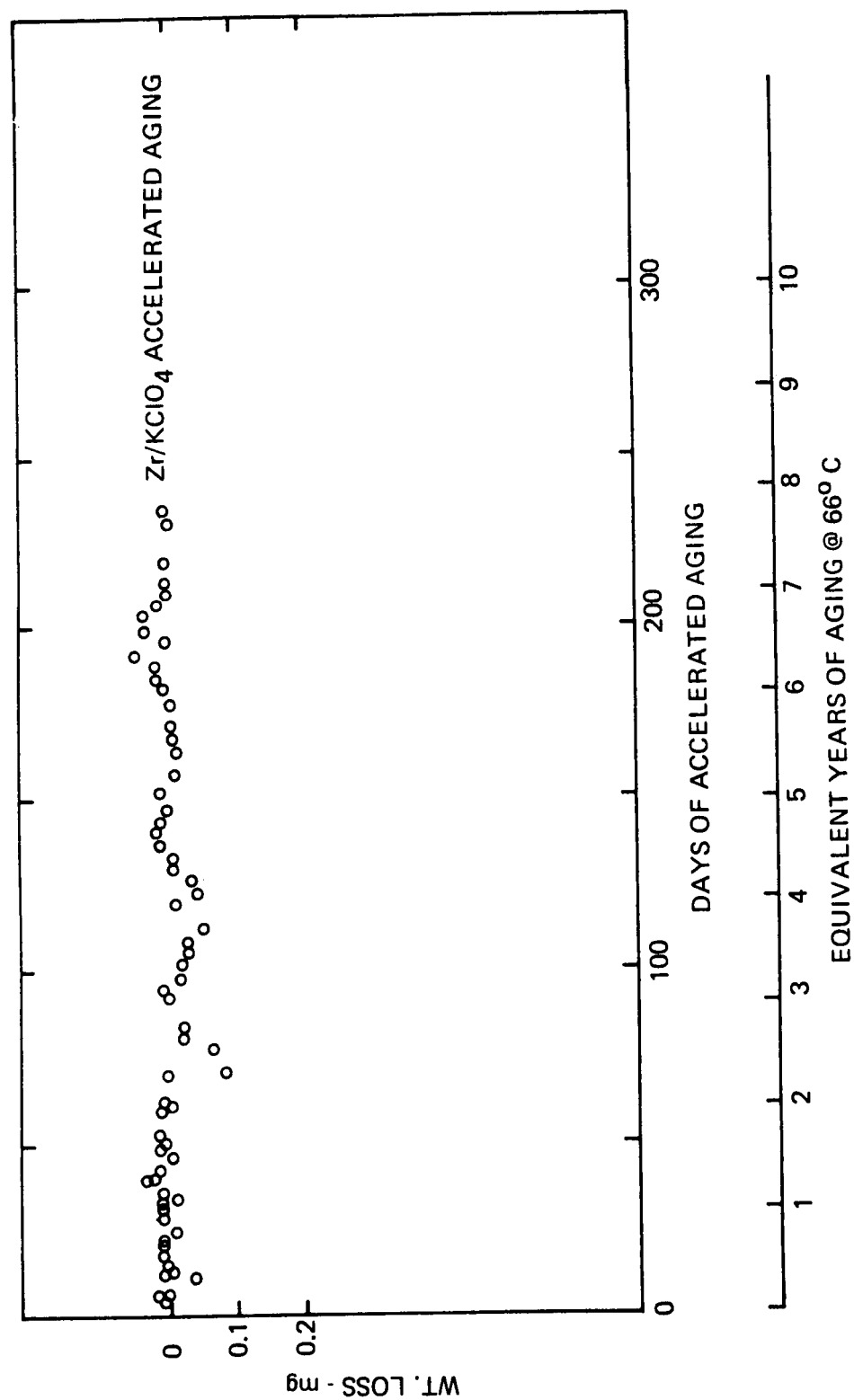


Figure 37. - Accelerated Aging Weight Loss for Zr/KClO₄

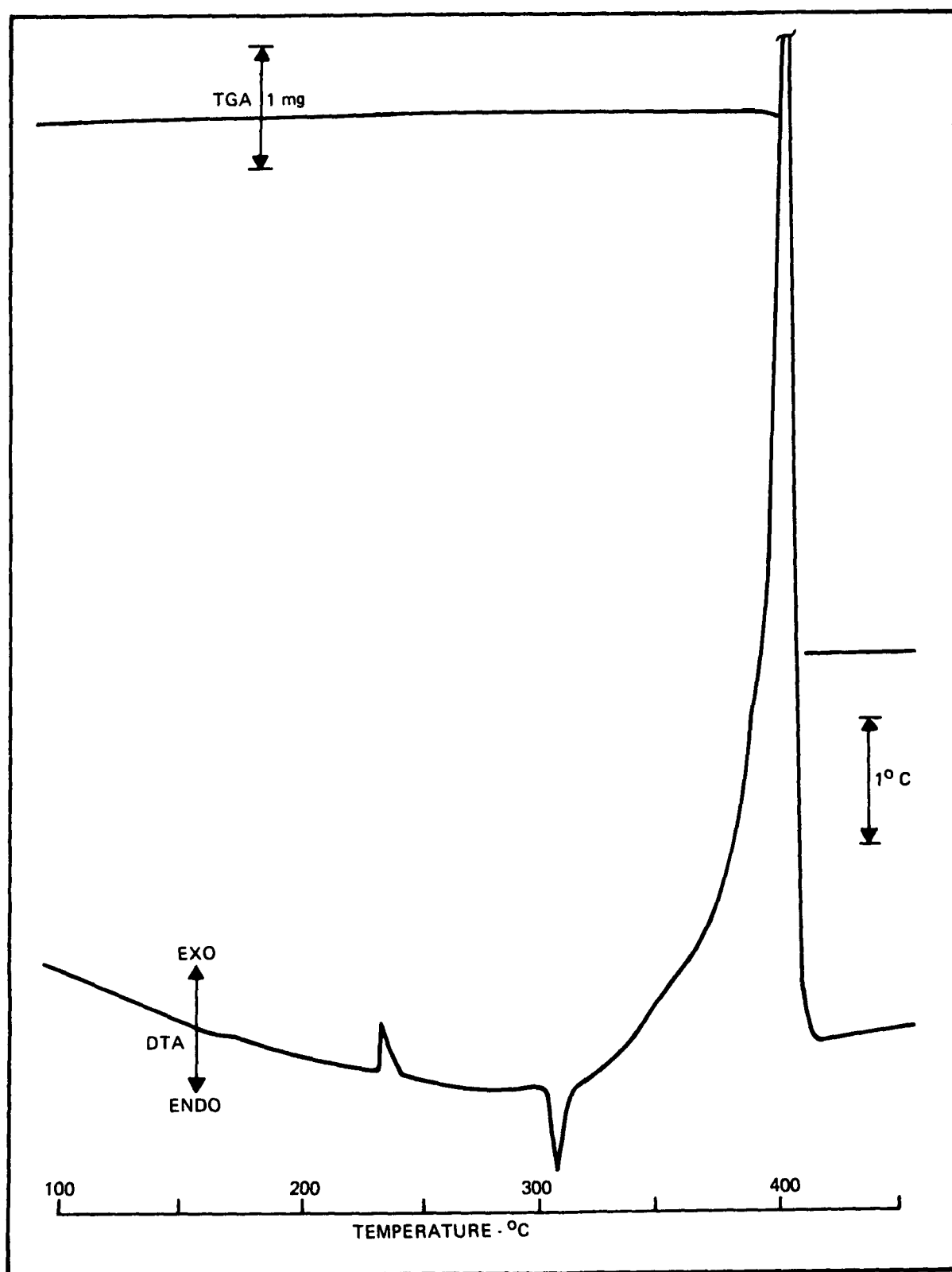


Figure 38. - Thermograph of Zr/KClO_4 After 183 Days Accelerated Aging

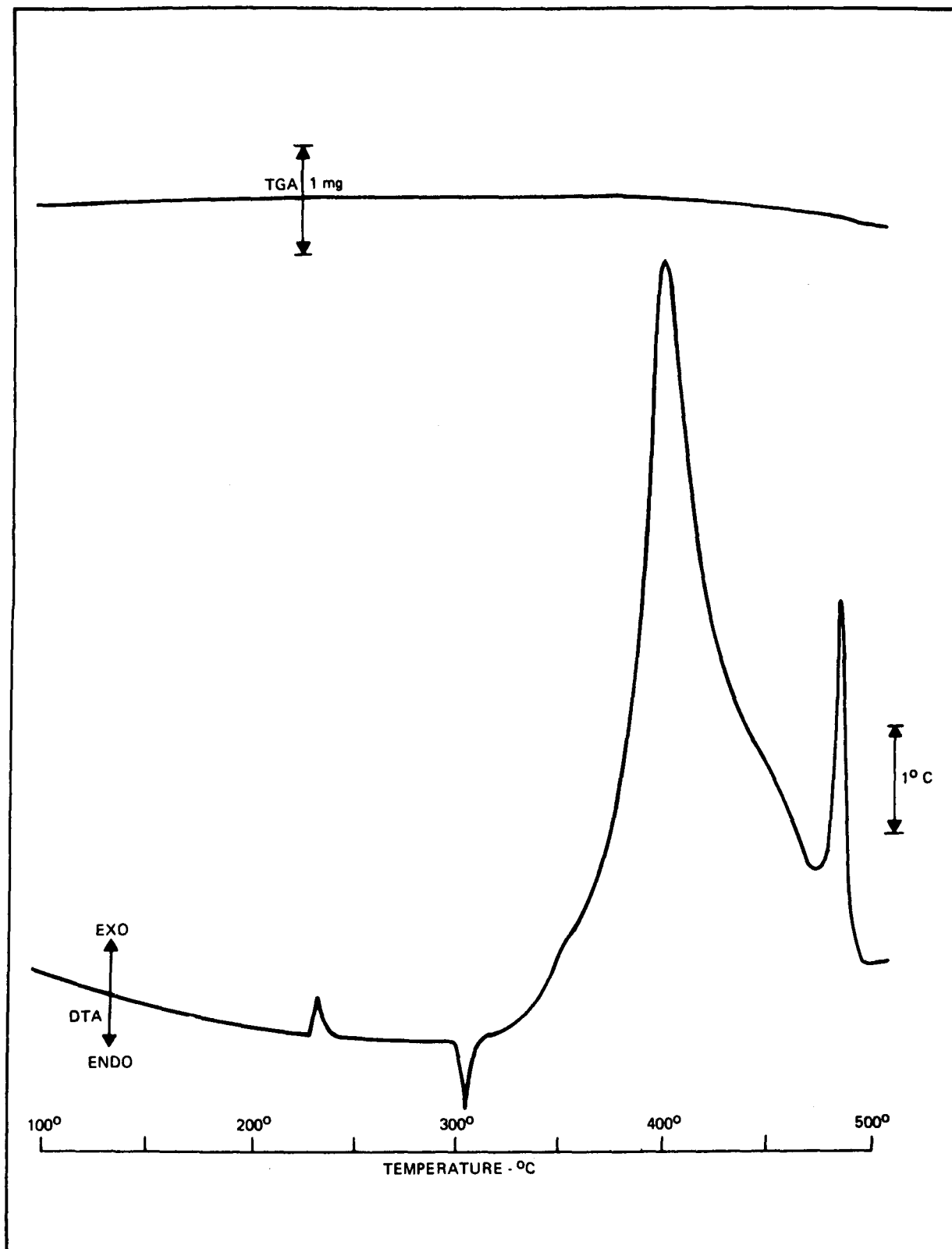


Figure 39. - Thermograph of Sterilized Zr/KClO_4 After 94 Days Accelerated Aging

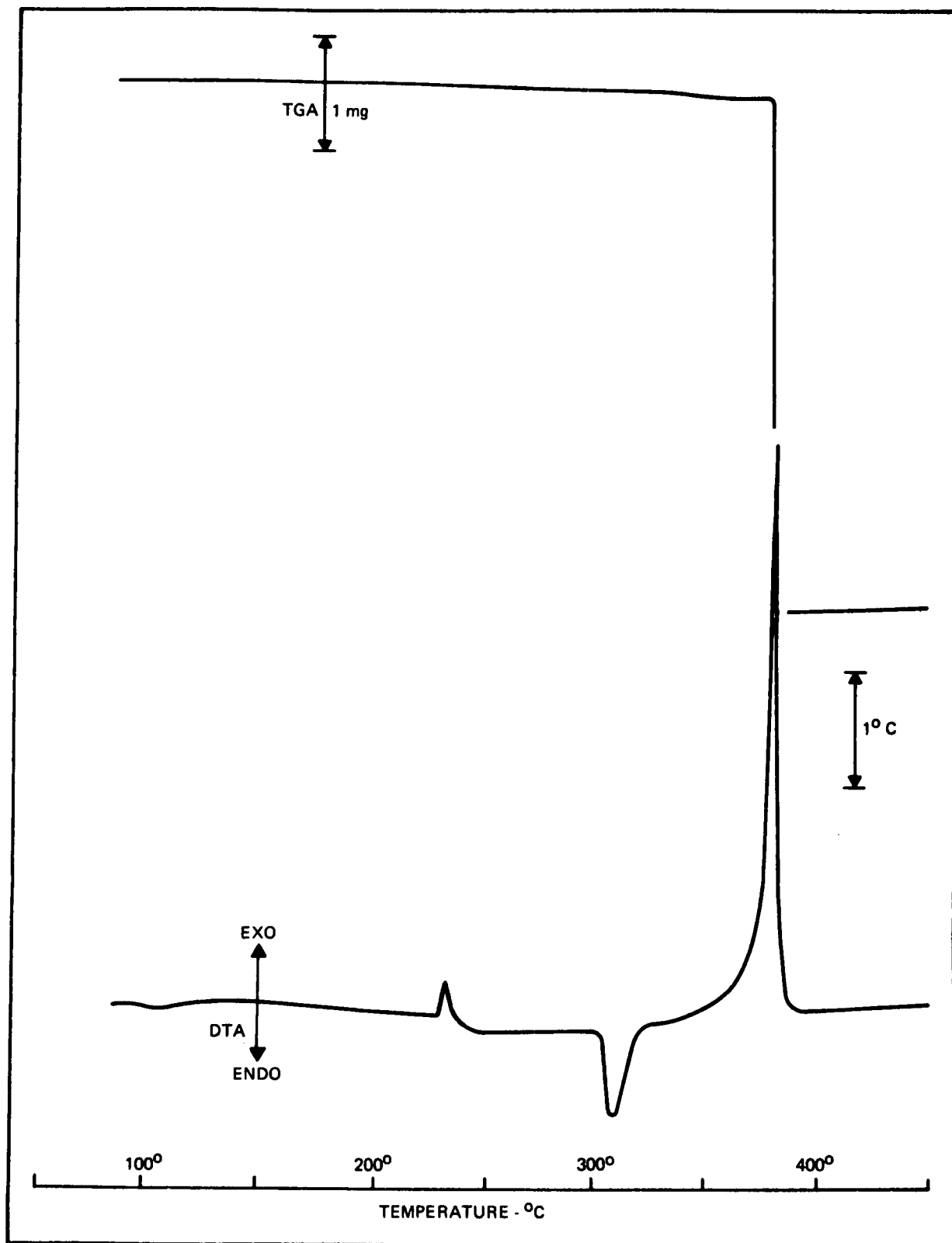


Figure 40. - Initial Thermograph for B/KClO₄

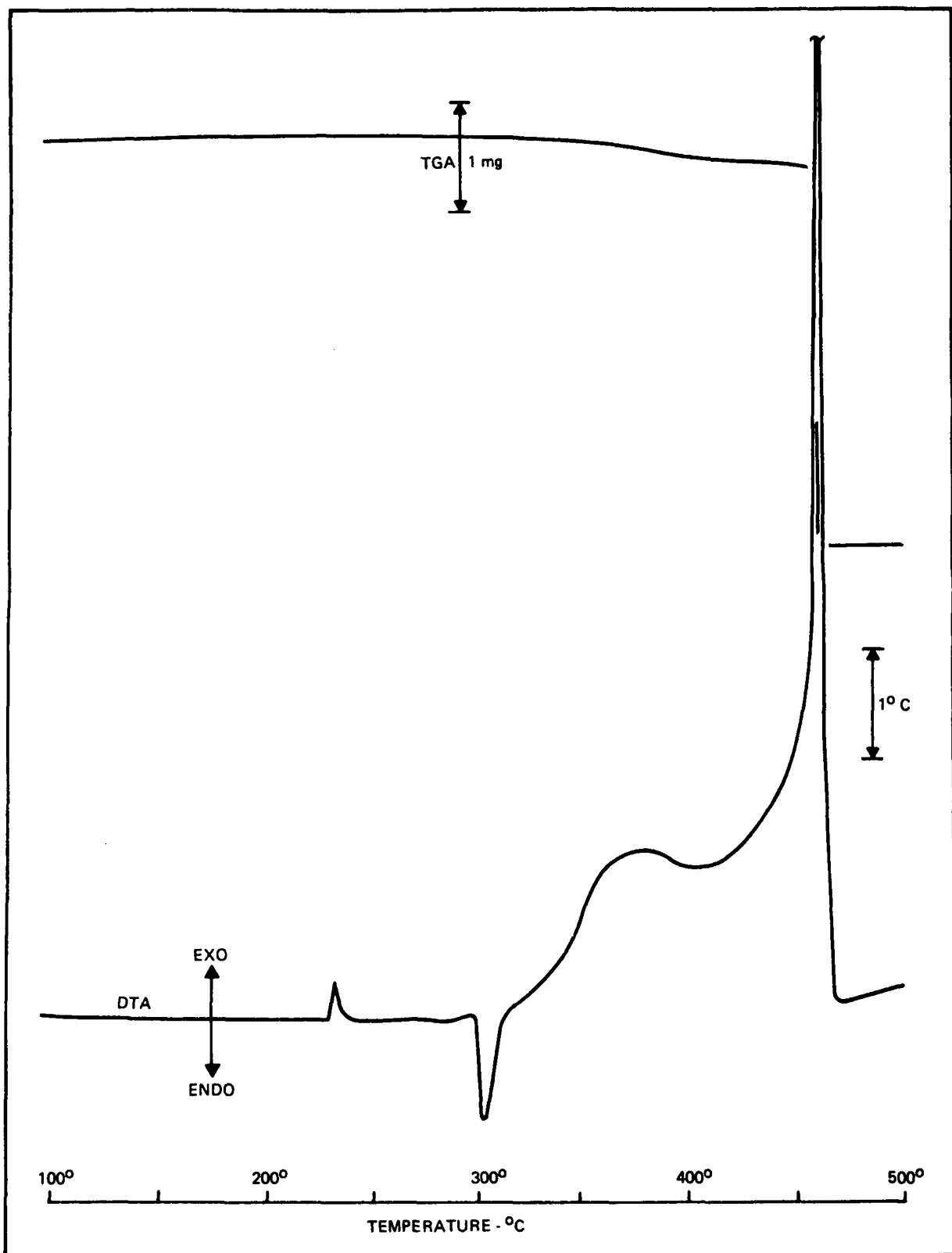


Figure 41. - Thermograph of $B/KClO_4$ After Two Sterilization Cycles

TABLE VIII. - THERMAL EVENTS OF STERILIZED AND UNSTERILIZED
B/KClO₄ PROPELLANT.

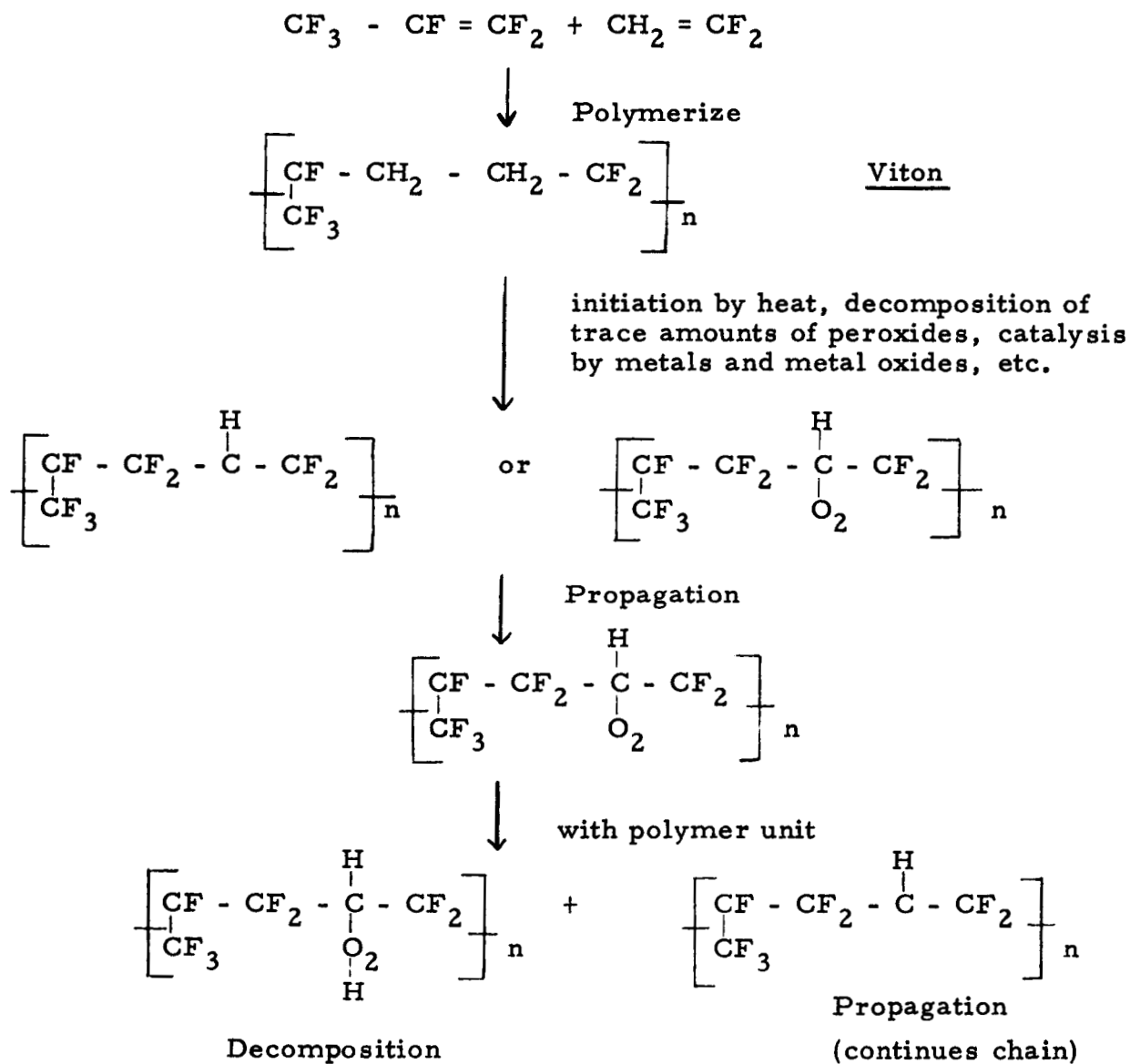
	Phase Change Endotherm (°C)	Decomposition Exotherms (°C)
Unsterilized	311	382
After 1 heat soak	311	368, 473
After 2 heat soaks	311	382, 461

TABLE IX. - WEIGHT LOSS (AS FRACTIONAL DECOMPOSITION α)
DURING STERILIZATION.

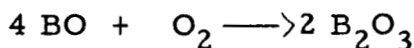
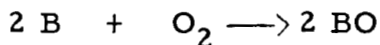
Fractional Decomposition (α)	Air Sterilization	Nitrogen Sterilization
0.1	54 min	46 min
0.2	2 hrs 12 min	12 hrs 2 min
0.3	4 hrs 3 min	22 hrs 54 min
0.4	6 hrs 49 min	36 hrs
0.5	11 hrs	57 hrs
0.6	18 hrs 12 min	

It is clear from this data that sterilization in nitrogen increases the stability of the propellant with respect to the obvious degradation in air. However, even in nitrogen the degradation is severe.

The cause of the observed degradation is undefined although we speculate that viton in the propellant environment of oxidizer, metal particles, iron oxide could decompose along a reaction path shown below:



The apparent anomaly of the propellant being more exothermic after sterilization is believed to be due to the burning of the boron during propellant combustion. During combustion it is highly probable that the boron is reacting in the gas phase along the following paths



and thus the energy of these reactions would not be recorded by DTA. During sterilization it is possible that BO can be formed in the solid propellant and its conversion to B_2O_3 could therefore be accomplished in the solid propellant during decomposition whereby the DTA will record this energy and exhibit a higher energy decomposition compared to the unsterilized propellant.

SEM photographs (Figures 42 and 43) indicate no morphology change in the material as a result of sterilization.

Sublimation measurements were conducted over the temperature range of 100° to 210° C for B/ $KClO_4$. Only at 200° and 210° C were measurable weight losses observed. A summary of these results appears in Table X.

TABLE X. - SUBLIMATION RESULTS FOR B/ $KClO_4$

Temperature $^\circ$ C	Wt. Loss Rate mg/ hr	G Sublimation Rate
200°	1.82×10^{-4}	7.66×10^{-11}
210°	8.0×10^{-4}	3.37×10^{-10}

Isothermal decomposition measurements were performed on B/ $KClO_4$ over the temperature range of 255° - 330° C. However, inconsistencies in the data, similar to those already discussed, prevented the derivation of accelerated-aging temperatures and rates. An activation energy of $7.2 \text{ kcal mole}^{-1}$ was measured for the open-air condition and $8.9 \text{ kcal mole}^{-1}$ was measured for the closed-volume air condition. But, when these values were used in conjunction with the rate constants measured under these two conditions to calculate rate constants at 66° C, the fractional decomposition (α) for one year at 66° C exceeded the value of 1. The data taken under the continuously pumped vacuum and closed volume vacuum are so confused that no results could be obtained.

Samples of B/ $KClO_4$ were subjected to accelerated aging in vacuum at 84° C, the same conditions used for the other materials. After 183 days of accelerated aging, the thermograph shown in Figure 44 was obtained. This figure indicates changes similar to those observed following sterilization. These changes were not observed in the thermograph taken after 117 days of accelerated aging.

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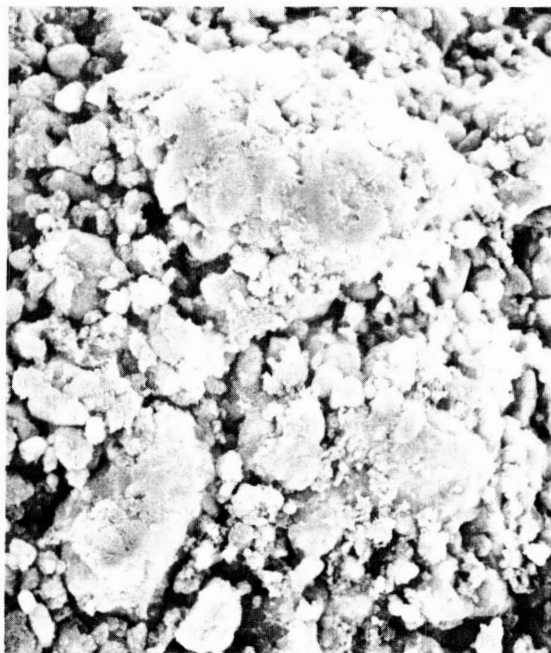


Figure 42. - B/KClO₄—Before Sterilization (600X)

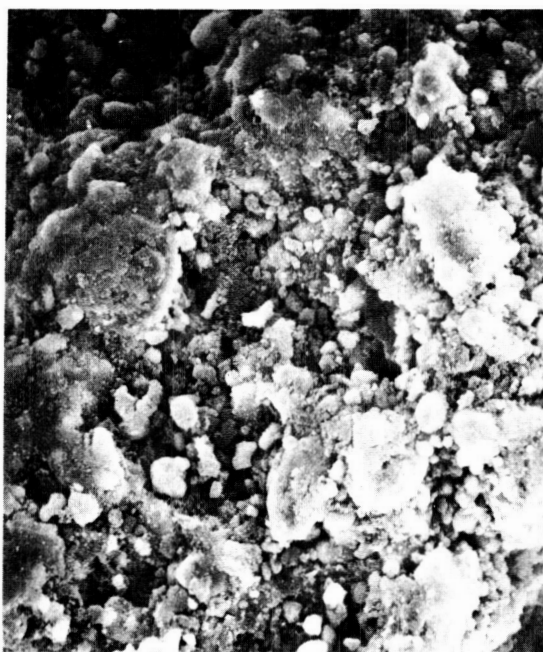


Figure 43. - B/KClO₄—After Sterilization (2X, 64 hr, 125° C) (600X)

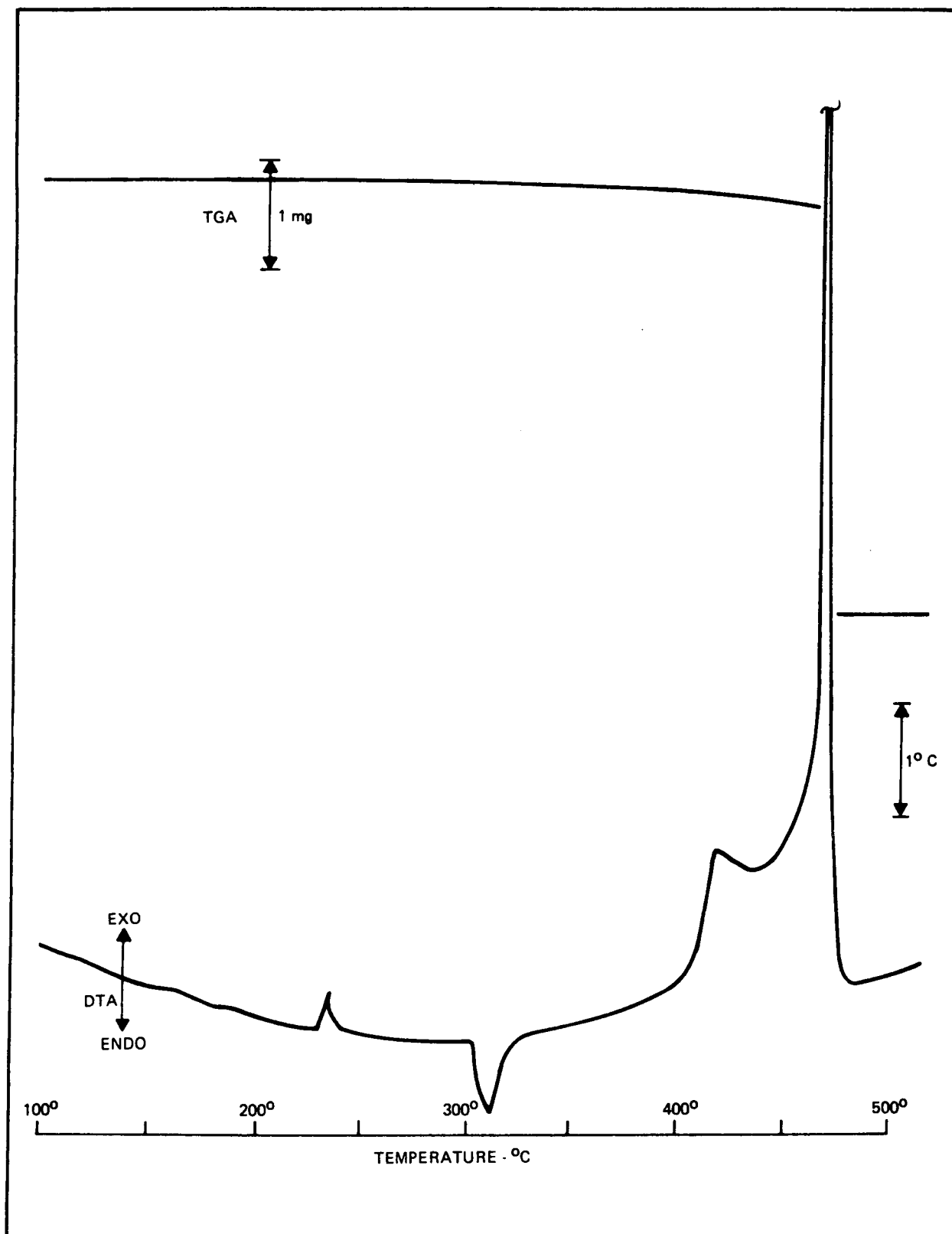


Figure 44. - Thermograph of $B/KClO_4$ After 183 Days Accelerated Aging

CONCLUSIONS

Based upon the results obtained from the sterilization tests, it would appear that HNS-IIA, pure PbN_6 , KDNBF, and Zr/KClO_4 are capable of withstanding two cycles at 125°C for 64 hours each, without causing measurable change in the thermal characteristics of the materials. Dextrinated PbN_6 and B/KClO_4 , however, do show significant changes in their thermal characteristics, even after only one sterilization cycle. In the case of dextrinated lead azide, sterilization appears to result in failure of the material to detonate with a corresponding decrease in weight loss and energy release. Whereas, B/KClO_4 apparently undergoes a mechanism change in the main decomposition process. If B/KClO_4 must be sterilized, it is recommended that functional testing be performed on the sterilized material to ascertain that important operational parameters are not affected by sterilization.

All of the materials (excepting KDNBF which was not tested) have sufficiently small sublimation rates and therefore, low vapor pressures so as to not constitute a problem by their use on extended length missions. However, it must be noted that the weight loss measured for dextrinated PbN_6 is believed to be the result of decomposition of the dextrin, rather than the result of sublimation.

Determination of the realistic accelerated aging parameters of a material through the use of isothermal decomposition studies is possible. However, under certain test conditions, the reaction kinetics of the decomposition may be masked by side effects (e.g., interaction of the decomposition products or back reaction of decomposition products with starting material, etc.)

The use of the accelerated aging parameters to predict the effect of aging on explosives and propellants has been demonstrated. And the results of these experiments indicate that HNS-IIA, and Zr/KClO_4 , unsterilized, are capable of withstanding up to ten years of deep space exposure at 66°C without measurable change in their thermal characteristics. Unsterilized pure PbN_6 and KDNBF exhibit small weight losses (less than 2%) but do not exhibit significant change in their thermographs. Unsterilized B/KClO_4 exhibits significant changes in its thermal characteristics, similar to those observed after sterilization, as a result of accelerated aging.

The accelerated aging of sterilized HNS-IIA over a 94-day period (equivalent to 3.1 years at 66°C) caused no detectable change in the thermograph of the material. However, sterilized pure PbN_6 and Zr/KClO_4 did exhibit changes in their thermographs after relatively short accelerated aging periods of 66 days (2.2 years) and 94 days (3.1 years), respectively. Changes in the sterilized pure PbN_6 after accelerated aging were similar to those observed following the sterilization of dextrinated PbN_6 . Sterilized Zr/KClO_4 following aging exhibited changes similar to those observed for B/KClO_4 (i.e., a decrease in the size of the main exothermic peak and the appearance of a second exothermic peak at higher temperature) but not to as

great a degree. One possible explanation for this difference in behavior between the sterilized and unsterilized material is that sterilization in air creates initiation sites (by decomposition, oxidation, etc.) which then enhances the decomposition during accelerated aging (see discussion under B/ KClO_4 results).

It should be noted that the objective of this program was to evaluate the effect of accelerated aging on the selected materials and to measure the changes produced. However, the establishment of criteria for or the determination of the degree of decomposition or change necessary to cause failure of a material in its functional performance was not within the scope of this program. Therefore, prior to the use of one of the materials under conditions which caused thermal characteristic changes, tests should be performed to verify that the changes observed do not affect functional performance of the material.

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